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Evaluation of Emulsion Stability. Effect of Tween Group Emulsifiers on Stability of o/w Type Emulsions[1]

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Examinations were made on the effect of Tween group emulsifiers, with combination of Span-20 and Tween-81 among them, to discuss the required HLB in detail, for o/w type emulsions with the use of various measurement methods.

Oil-in-water emulsions were prepared containing 45% of dispersed phase. The emulsifiers used were commerical grade nonionic surfactants of four Tweens and Span-20, and the oil used was a mineral oil. Emulsion was formed by agitation, and emulsion stability was measured with four apparatuses, measuring cylinder, Coulter counter, turbidimeter, and rheometer. Following results were obtained,

1) The rate of separation was affected largely by the kind of emulsifiers, which increased in the order of Tween-81, Tween-81+Span-20, Tween-85, Tween-20, and Tween-21.

2) The o/w emulsion showed the maximum value of droplet number at characteristic HLB value equal to 10.0.

3) Viscosity of the emulsion increased with the increase of emulsifier concentration.

Keywords——agitator; Coulter counter; emulsifier; emulsion stability; HLB value; rheometer; revolution number; separation rate of drainage phase; turbidimeter; viscosity

Emulsion is considered as a dispersion of one liquid in another; that is, a two-phase system from the thermodynamic point of view. The dispersed phase is consisted of microscopic droplets usually within the size range of 0.1 to 100 μm in diameter. Such dispersions are never completely stable in the absolute sense, because the interface between two phases is the seat of surface free energy, and if two droplets join together there is a net reduction in interfacial area. Hence, coalescence of droplets is a thermodynamically spontaneous process and therefore emulsification does not occur spontaneously.[3]

In discussing emulsion stability, it is essential to distinguish "breaking," "creaming," and "flocculation," because any or all of these phenomena may occur after the emulsion has been prepared. Breaking is the spontaneous joining of small droplets in the emulsion to form larger ones, leading ultimately to two separate liquid layers. Creaming is the rise of dispersed droplets by the effect of gravity, the droplets remaining separate when the dispersed phase is of smaller density than the continuous phase. Finally, flocculation is the sticking together of droplets in the formation of three-dimensional clusters without coalescence of individual droplets.

Among many factors affecting emulsion stability, the Hydrophile Lypophile Balance (HLB) system for selecting emulsifiers will be considered as one of the most important factors. In the HLB concept[4-6] which developed initially from observations by Griffin, the HLB

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1) T. Kubo, A. Takamura, and S. Noro, presented at the 98th Annual Meeting of the Pharmaceutical Society of Japan, Okayama, April, 1978.
2) Location: *a) 1-22-1, Yato-cho, Tanashi-shi, Tokyo 188, Japan. b) 12, Ichigaya Funagawara-machi, Shinjuku-ku, Tokyo 162, Japan.*
3) P. Sherman, "Emulsion Science," Academic Press, London, 1968, p. 77.
4) W.C. Griffin, *J. Soc. Cosmet. Chem.*, **1**, 311 (1949).
5) W.C. Griffin, *J. Soc. Cosmet. Chem.*, **5**, 249 (1954).
6) W.C. Griffin, *Off. Dig. Fed. Paint Varn. Prod. Clubs.*, **28**, 446 (1956).

value is considered a function of the weight percentage of hydrophilic portion of the molecule of a nonionic surfactant. Furthermore, Shinoda[7,8] pointed out that HLB concept depends on the balance of the emulsifiers at the oil-water interface, and that HLB would also depend on the nature of the oil phase and on the additives in the aqueous and oil phases.

There are a few ways to characterize emulsifier efficiency for emulsion stability. For example, one of the ways used was determine the rate of separation of dispersed phase from emulsion stored in a closed glass cylinder.[9] In other ways, the Coulter counter, turbidimeter, and rheometer will be excellent apparatuses to evaluate systematically or quantitatively the influence of HLB of emulsifiers on emulsion stability.

It was the purpose of the present work to investigate the effect of Tween emulsifiers and a combination of Span-20 and Tween-81, to discuss the required HLB in detail, for o/w type emulsions with the use of above mentioned measurement methods. In addition, we attempted to evaluate some of the factors which influence emulsion stability.

Experimental

Equipments——A sketch of the apparatus used is shown in Fig. 1. The clear acrylate resin agitation tank with 4 baffles was 150 mm in diameter and 210 mm deep. A stainless-steel agitation impeller of 49.0 mm was of the standard Rushton type with 6 blades.[10] The tank was surrounded by a water jacket in order to keep the temperature of the liquid at 20.0°. Revolution number of impeller was constant at 812 rpm. Agitation period was 6, 20, 60, and 120 min.

Preparation of Emulsions——Oil-in-water emulsions contained 45.0% of dispersed phase. The emulsifiers used were commercial grade Tweens; Tween-81, Tween-85, Tween-21, and Tween-20, and Span-20 as nonionic surfactants (Kao-Atlas Co., Tokyo), and the oil used was a mineral oil. In preparation of these emulsions, the emulsifiers used to prepare the o/w emulsions were a mixture of Tween and Span blended together and Tween alone so as to give HLB values within the range of 8.5—16.5. Before starting emulsification, the surfactant was always dissolved in mineral oil. The total emulsifier concentration in each emulsion was varied within the range of 0.5 to 10%.

Interfacial tension between oil and water was measured by the ring method and specific gravity was measured by a hydrometer at $20.0 \pm 0.1°$.[11] Physical properties at each emulsifying experiment are summarized in Table I.

Experimental Procedure——The experiments were carried out under the following conditions:

(1) The values of HLB were 9.3, 9.8, 10.0, 11.0, 13.3, or 16.9.

(2) The concentration of each surfactant was kept at 5.0%, for the evaluation of emulsion stability at the same level.

(3) The revolution number was kept constant at 812 rpm.

(4) Samplings were made at 6, 20, 60, and 120 min after agitation started.

The agitation tank was filled with 1375 ml of distilled water as a continuous phase. The impeller was set in the center of the tank. On the middle of the impeller was gently placed 1125 ml of a mineral oil as a dispersed phase. The total liquid volume was 2500 ml. After agitation started, the emulsified liquid was sampled with a glass tube (5 mm) at regular intervals. Each sample was used to evaluate the emulsion stability by four measurement methods.

Measurement of Emulsion Stability——Emulsion stability was measured with four apparatuses such as measuring cylinder, Coulter counter, turbidimeter, and rheometer as shown in Fig. 1.

First, stability of the emulsion was measured in terms of the degree of separation;[12] the emulsion was left standing in a glass tube at room temperature for 3 days and then height of a drainage phase appearing in the lower part of the tube was measured as the degree of separation.

Second, stability of the emulsion was examined in terms of the number of emulsion droplets[13] by the Coulter counter (Model ZB, Coulter Electronics Co., Florida U.S.A.). In the present experiments, the tube having a 50 μm aperture was chosen and 1% NaCl in water (dielectric constant, 550 ohm/cm) was used as an electrolyte.

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7) K. Shinoda, *Nippon Kagaku Zasshi*, **39**, 435 (1968).
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9) T. Mitsui, Y. Machida, and F. Harusawa, *Am. Cosmet. and Perfum.*, **87**, 33 (1972).
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12) T. Mitsui, Y. Machida, and F. Harusawa, *Bull. Chem. Soc. Jpn.*, **43**, 3044 (1970).
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Third, stability of emulsion was evaluated by the relative turbidity with PT-201 type turbidimeter of Nihon Seimitsu Kogaku Co., Tokyo.[14] Since the turbidimeter adopted the integration sphere method of electrophotometer, the turbidity can be measured exactly. In this measurement, emulsion formed by agitation was poured first into a beaker. In succession, some definite volume of the emulsion was sampled rapidly with a pipette and diluted with distilled water until 200 ppm concentration.

Finally, stability of emulsion was evaluated in terms of rheological properties with RM-1 type rheometer of Shimadzu Seisakusho, Kyoto.

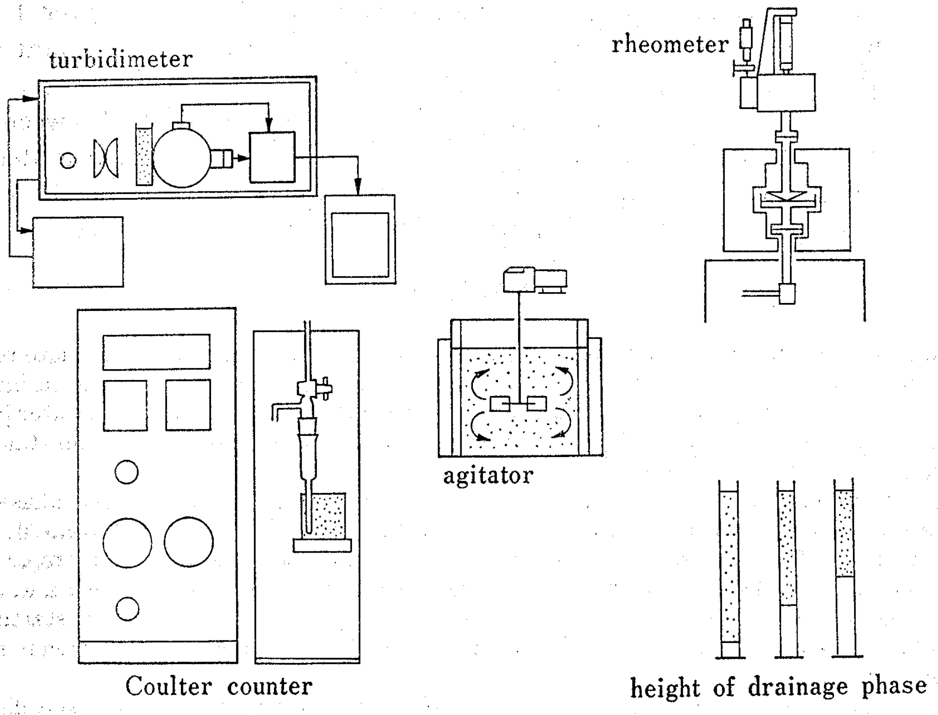

Fig. 1. Measurement Methods of Emulsion Stability

TABLE I. Physical Properties under Each Emulsifying Experiment

Emulsifiers name	Chemical name	Radical number of polyoxyethylene	Saponification value	HLB
Span-20 +	Sorbitan monolaurate	—	158—170	9.3
Tween-81[a]	Polyoxyethylene sorbitan monooleate	5	96—104	
Span-20 +	Sorbitan monolaurate	—	158—170	9.8
Tween-81[b]	Polyoxyethylene sorbitan monooleate	5	96—104	
Tween-81	Polyoxyethylene sorbitan monooleate	5	96—104	10.0
Tween-85	Polyoxyethylene sorbitan trioleate	20	80— 95	11.0
Tween-21	Polyoxyethylene sorbitan monolaurate	4	120—115	13.3
Tween-20	Polyoxyethylene sorbitan monolaurate	20	40— 50	16.9

a) 1:1 for Span-20: Tween-81 blends.
b) 1:6 for Span-20: Tween-81 blends.
Dispersed phase: mineral oil.
Continuous phase: distilled water.
Agitation time: 120 min.
Revolution number: 812 rpm.

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14) A. Takamura, S. Noro, S. Ando, and M. Koishi, *Chem. Pharm. Bull.* (Tokyo), **25**, 2144 (1977).

Results and Discussion

Influence of HLB Values of Different Emulsifiers on Emulsion Stability

The two effects of the kinds of emulsifying agent and the agitation period of emulsification on both the height of drainage phase and the stability of resultant emulsions were studied. The HLB values varied from 8.5 to 16.5 with various emulsifiers. These results are shown in Fig. 2. In spite of the presence of an emulsifier, in this case, the height of drainage phase increased rapidly at the very early stage after preparation of the emulsion and these initial slopes became approximately straight lines. Subsequently, these curves levelled off as the standing time increased. The levelling-off was observed after about 100 to 200 min. The rate of separation of dispersed phase from emulsions decreased with increase of agitation time. Generally, stability of emulsions is proportional to the size of dispersed droplets and the difference of specific gravity between oil and water phases. Accordingly, the degree of separation became smaller as the droplet size and the difference between specific gravity of two phases decreased.

Figure 3 shows comparative results for the change in height of the drainage phase with standing time on four different emulsifiers. The rate of separation was affected largely by the kind of emulsifiers, and it was found to increase in the order of Tween-81, Tween-81+Span-20, Tween-85, Tween-20, and Tween-21.

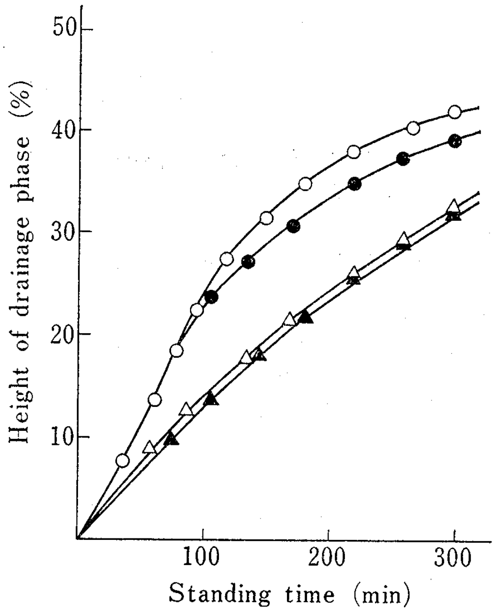

Fig. 2. Relationships between Height of Drainage Phase and Standing Time

Agitation time ○: 6 min, ●: 20 min, △: 60 min, ▲: 120 min.
Emulsifier: Tween-85 (HLB=11.0).
Concentration: 5.0%.
Equipment: agitator.
Revolution number: 812 rpm.

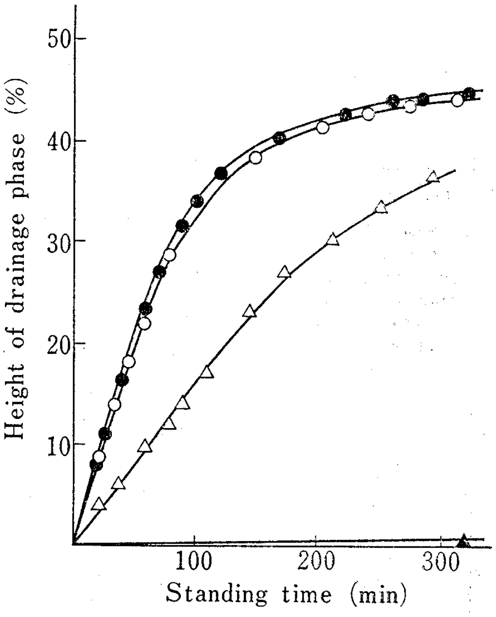

Fig. 3. Change of Height of Drainage Phase with Time on Different Emulsifiers

○: Tween-20, ●: Tween-21, △: Tween-85, ▲: Tween-81+Span-20 (HLB=9.8).
Concentration of emulsifiers: 5.0%.
Equipment: agitator.
Revolution number: 812 rpm.
Agitation time: 60 min.

The influence of HLB value on the number of droplets is shown in Fig. 4 for o/w emulsions stabilized by one of four kinds of Tween and one Span emulsifiers. The number of droplets, which is counted among the quantitative criteria of emulsion stability, was measured immediately by the Coulter counter after the emulsion was prepared by agitation. It was readily observed that HLB values of the emulsifiers exerted a large influence on the number of droplets. The o/w emulsion showed the maximum value at characteristic HLB value equal to 10.0. The number of droplets fell rather sharply on either side of the optimum HLB. The number decreased in the order of Tween-81, Tween-81+Tween-85, Tween-85, Tween-81+Span-20, Tween21, Tween-20.

The influence of HLB value on the turbidity of emulsion is shown in Fig. 5. It was found from this graph that the plotted curve showed the maximum turbidity at a characteristic HLB value of 10.0. The value of turbidity fell rather sharply on either side of the optimum HLB, as observed in Fig. 5. That is, the turbidity of emulsion sample attained the maximum value at a characteristic HLB which corresponded reasonably well with the point of maximum droplet number. Thus, it might be suggested that there are some interrelational function between the turbidity of emulsion and the size of dispersed droplets. Finally, it might be thought that HLB value of emulsifiers is a very effective factor in stabilizing an emulsion.

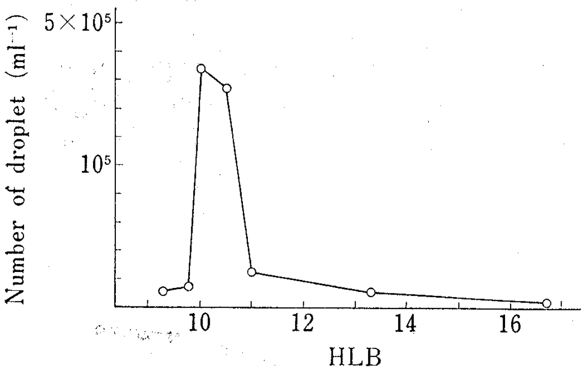

Fig. 4. Relation between Number of Droplet and HLB Value

Dispersed phase: mineral oil.
Continuous phase: distilled water.
Concentration of dispersed phase: 45%.
Equipment: agitator.
Revolution number: 812 rpm.
Agitation time: 60 min.

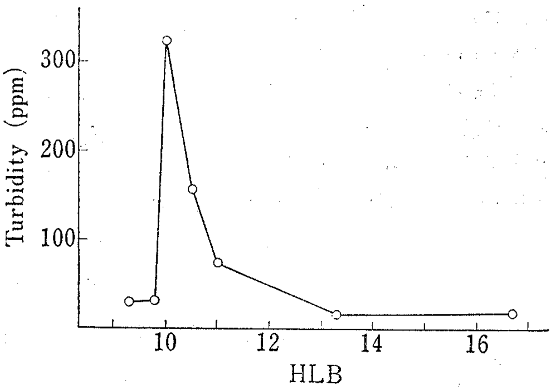

Fig. 5. Relation between Turbidity and HLB Value

Dispersed phase: mineral oil.
Continuous phase: distilled water.
Concentration of dispersed phase: 45%.
Equipment: agitator.
Revolution number: 812 rpm.
Agitation time: 60 min.

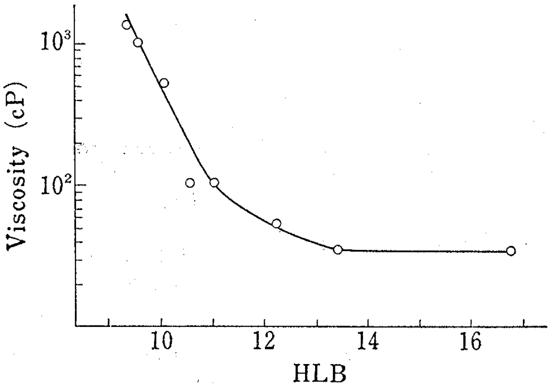

Fig. 6. Relation between Viscosity and HLB Value

Dispersed phase: mineral oil.
Continuous phase: distilled water.
Concentration of dispersed phase: 45%.
Equipment: agitator.
Revolution number: 812 rpm.
Agitation time: 60 min.
Shear rate: 7.5 sec^{-1}.

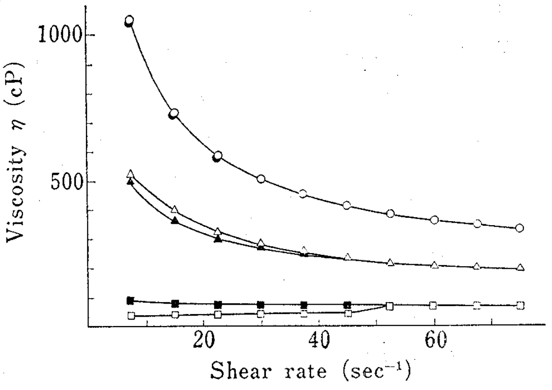

Fig. 7. Rheograms of Emulsion prepared by Different Emulsifiers

Tween-81+Span-20 ○: upward stress curve,
●: downward stress curve.
Tween-81 △: upward stress curve,
▲: downward stress curve.
Tween-20 □: upward stress curve,
■: downward stress curve.
Dispersed phase: mineral oil.
Continuous phase: distilled water.
Concentration of dispersed phase: 45%.
Concentration of emulsifier: 5.0%.

The influence of HLB value on the viscosity of emulsion stabilized by emulsifiers is shown in Fig. 6. In this experiment, the shear rate was kept constant at 7.5 $\sec^{-1}$. Collective logarithmic plots of viscosity against HLB value indicated curvilinear relationship in the range of HLB 8.5 to 16.5. The observation that can be seen in Fig. 6 was in general agreement with the both observations drawn in Fig. 4 and 5 when HLB value was higher than 10.0. In particular, viscosity of an emulsion decreased markedly with increase of HLB value from 10.0 to 10.5. On the contrary, it was found that viscosity of an emulsion did not decrease but rather increased when HLB values became below 10.0. This may be interpreted as the viscosity of emulsion was affected by the phase inversion phenomenon.

When comparing the flow behaviors of two or more different emulsions, their viscosity should be measured over a wide range of shear rates. "Single point" determinations can lead to incorrect conclusions. On dealing with non-Newtonian flow, the rate of shear at which viscosity is determined should be quoted. The gradient, $\Delta f/\Delta(du/dx)$, of the linear portion of non-Newtonian flow curves is referred to as the "apparent viscosity." Rheograms of emulsion prepared by three different emulsifiers are shown in Fig. 7. The curves showing the relationship between η and du/dx were not remain constant, but η was first decreased markedly and then decreased with increase of du/dx. When a low steady shear was applied to concentrated emulsions, it was often found that a steady stress did not develop instantly. This phenomenon is referred to as thixotropy. It was found from Fig. 7 that the hysteresis effect appeared in a thixotropic emulsion produced by Tween-20 and Tween-81. For o/w emulsions, viscosity decreased in the order of a mixture of Tween-81 and Span-20 (HLB=9.8), Tween-81 (HLB=10.0), and Tween-20 (HLB=16.5).

Influence of Concentration of Emulsifiers for Emulsion Stability

Effect of concentration of an emulsifier on emulsion stability was studied at different concentrations. Tween-81 (HLB=10.0) was selected as a typical emulsifier because optimum stability was obtained with it, as seen in Fig. 2 to 7.

The influence of concentrations on the height of drainage phase is shown in Fig. 8. For both concentrations of 0.5 and 1.0%, the height observed increased rapidly at the very early stage after preparation of the emulsion and then the height levelled off as the standing time elapsed. In general, the rate of drainage became slower as the concentration of Tween-81 increased. The drainage phase did not appear at all when the concentration was over 2.0% in spite of the fact that the emulsion was kept for 7 days after preparation. Consequently, it would be postulated that emulsifier molecules associated and saturated at the oil–water interface, that is, on the surface of dispersed droplets, when the concentration of Tween-81 reached about 2.0%. As a result, the stable adsorbed monolayer was formed at the oil–water interface and acted to decrease the interfacial tension between them.

The influence of concentration of Tween-81 on the number of droplets was studied for o/w emulsions. Fig. 9 illustrates the dependence of droplet number on the concentration between 0.5 and 10.0%. These are plotted on a semilogarithmic graph paper so that all data can be fitted into a single graph. Increased ratio of droplet number was slight by curvilinear below 2.0% concentration. Thereafter, the droplet number increased markedly with increasing concentrations.

The influence of concentration on Tween-81 on the turbidity of emulsion is shown in Fig. 10. This relation very closely agreed with the result shown in Fig. 9. It is suggested that there might be some correlation between the turbidity of emulsion and the size of emulsion droplets. It might be said that the concentration of emulsifiers was highly effective in stabilizing an emulsion.

Figure 11 illustrates how viscosity η for o/w emulsions increases when the concentration of Tween-81 rises from 0.5 to 7.0%. The viscosity values were plotted on a logarithmic graph paper so that all data were fitted into a single graph.

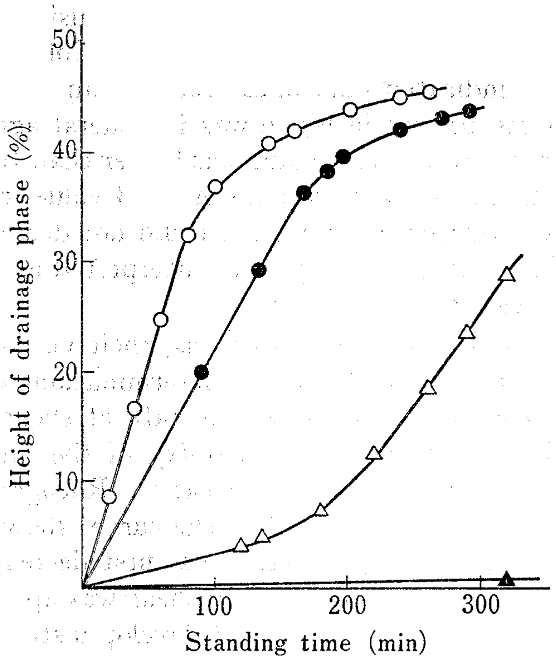

Fig. 8. Change of Height of Drainage Phase with Time at Different Concentration of Tween-81

○: 0.5%, ●: 1.0%, △: 1.5%, ▲: 1.8%.
Dispersed phase: mineral oil.
Continuous phase: distilled water.
Concentration of dispersed phase: 45%.
Equipment: agitator.
Revolution number: 812 rpm.
Agitation time: 60 min.

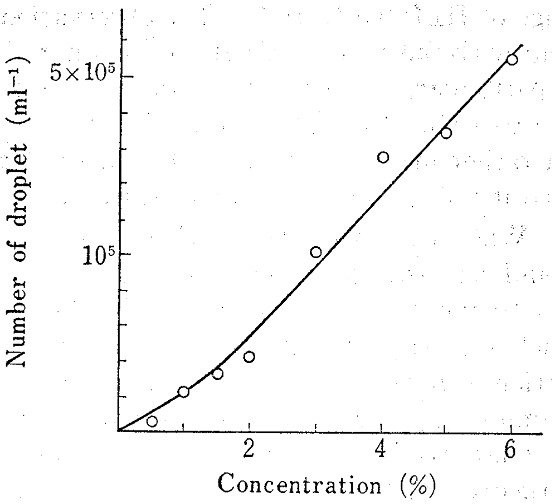

Fig. 9. Relation between Number of Droplet and Concentration of Tween-81

Dispersed phase: mineral oil.
Continuous phase: distilled water.
Concentration of dispersed phase: 45%.
Equipment: agitator.
Revolution number: 812 rpm.
Agitation time: 60 min.

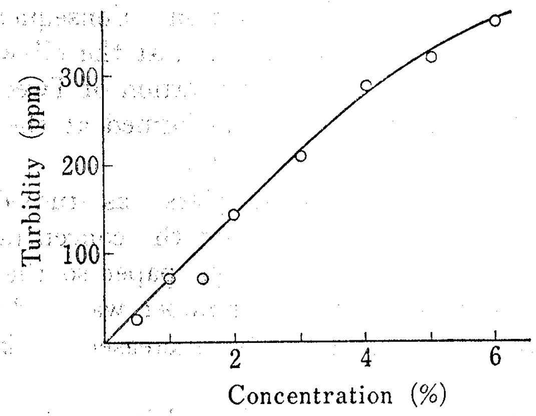

Fig. 10. Relation between Turbidity and Concentration of Tween-81

Dispersed phase: mineral oil.
Continuous phase: distilled water.
Concentration of dispersed phase: 45%.
Equipment: agitator.
Revolution number: 812 rpm.
Agitation time: 60 min.

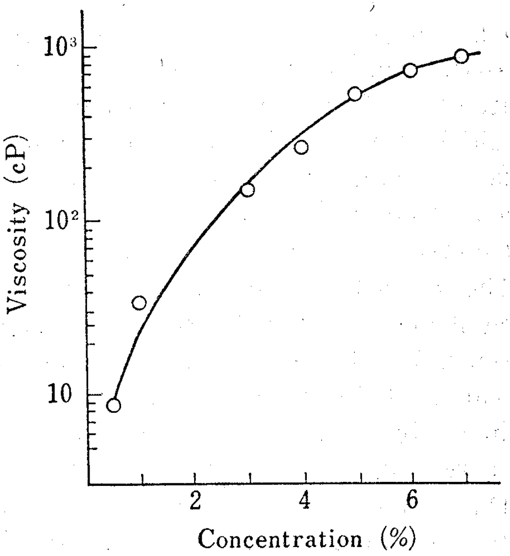

Fig. 11. Effect of concentration of Tween-81 to Viscosity of Emulsion

Dispersed phase: mineral oil.
Continuous phase: distilled water.
Concentration of dispersed phase: 45%.
Equipment: agitator.
Revolution number: 812 rpm.
Agitation time: 60 min.

The increased viscosity due to high emulsifier concentration has often been taken responsible for increasing the emulsifier adsorption around the surface of a droplet. While this may be true in some instances, it is unlikely that the adsorbed layer is more than one molecule thick with many other emulsifiers. As soon as a compact monomolecular layer has formed around the droplet in emulsions prepared with these emulsifiers, all excess emulsifier molecules associate to form micelles in the continuous phase. These micelles immobilize the continuous phase fluid within their interior in much the same way as soap micelles do in aqueous liquid. In bulk solutions of emulsifiers this is reflected in the non-linearity of the viscosity-concentration graph, but an additional effect appears in emulsions. Immobilization of the continuous phase alters the volume ratio of dispersed phase to "free" continuous phase, thereby producing a corresponding increase in viscosity. The greater the excess of emulsifier present, the greater is the volume of continuous phase immobilized.