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Effect of Homogenization Conditions on the Physicochemical Properties of Emulsion Bases

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The effects of the first pressure and/or number of passes through the homogenizer, and pre-agitation by an agitator, on the physical properties of emulsion bases were investigated.

The first pressure of the homogenizer was varied in the range of 130 to 490 kg/cm^2, and the second pressure was kept constant at 60 kg/cm^2. Emulsifiers used were commercial grade Tween 80 and Span 20. Oil and water phases were liquid paraffin and distilled water, respectively.

Emulsion stability was evaluated in terms of the following three physicochemical parameters: (1) particle diameter, (2) separation rate of water phase, (3) rheological properties of emulsion products. The following results were obtained. (1) With increases in agitation time and in intensity of agitation, the particle diameter of the emulsion became smaller. (2) The viscosity of emulsion prepared in the homogenizer increased remarkably with increase in the number of passes through the homogenizer. (3) The particle diameter of the emulsion was greatly decreased by the homogenizer only at the first pass. (4) Pre-agitation with an agitator is very useful for the preparation of emulsion products by means of a homogenizer.

Keywords——agitator; Coulter nanosizer; emulsifier; emulsion stability; homogenizer; particle diameter; pre-agitation; rheometer; viscosity

In order to prepare a stable emulsion, it is necessary to take into account not only the material conditions, such as the selection of emulsifier, the concentration of emulsifier or oil phase, the additives and so on, but also the machine conditions, such as the type of emulsifying machine, emulsifying time, agitation intensity and so on.

The homogenizer is useful in diverse fields of emulsification, in the food, pharmaceutical, cosmetics, and chemical industries.[1)] Although many reports on the selection[2)] of the best emulsifier to stabilize emulsions and the additives[3)] in an aqueous phase or oil phase have already been published, few reports have dealt with the conditions of mechanical agitation by the homogenizer.

We have already discussed how to select the best emulsifier for a liquid paraffin as an oil phase,[4)] and how to obtain high stability of w/o type emulsion prepared by the use of an agitator and a homogenizer with natural emulsifier.[5)] However, the effect of homogenization conditions on the formation of emulsion was not examined in detail. In the present work, o/w type emulsion, which is a dispersion of microscopic oil droplets in a water phase, was prepared by the use of an agitator and a homogenizer. The purpose of this work was to investigate the effects of the first pressure and/or the number of passes through the homogenizer on the physicochemical properties of the emulsion base. In addition, the effect of pre-agitation conditions in the agitator was studied.

Experimental

Equipment——A sketch of the apparatus used for the preparation of emulsions was presented in our previous paper.[6)] The clear acrylate resin agitation tank with 4 baffles was 150 mm in diameter and 210 mm in depth. The 49.0 mm long stainless-steel agitation impeller was a standard Rushton type with 6 blades. The tank was sealed with an acrylate resin disk to prevent the access of air, and it was surrounded by a water jacket in order to keep the temperature at 20.0 °C.

The homogenizer used was a type 15M-8TA machine from Goulin Co., U.S.A. Dispersion of the material to be emulsified occurs not only while the materials pass through the opening between the valve and the seat, but also when the resulting emulsion impinges against the retaining wall which surrounds the valve. Homogenizers were connected for multi-stage dispersion. Thus, the first stage of homogenization was usually carried out at high pressure, producing finely dispersed droplets, although they clumped. The second stage of homogenization, a lower pressure, broke up the clumps and produced emulsions of lower viscosity.

Materials——The emulsifiers used were commercial grade polyoxyethylene sorbitan monooleate (Tween 80) and sorbitan monolaurate (Span 20). The HLB value was adjusted to 11.0 and the emulsifier concentration in each emulsion varied within the range of 0.1 to 5.1% by weight. The dispersed phase material used was a liquid paraffin, and the continuous phase material was distilled water.

Procedure——Before starting emulsification, Tween was always dissolved in the aqueous phase, and Span in the oil phase.

The agitation tank was filled with 1375 g of distilled water as a continuous phase. The impeller was placed in the center of the tank. Liquid paraffin (945 g) was gently placed on the middle of the impeller as a dispersed phase. Before mixing, the tank was sealed with an acrylate resin disk to exclude air. The rate of revolution of the impeller was selected in the range of 530 to 1354 rpm, and samples were taken in the range of 6 to 120 min after the start of agitation.

The resulting coarse emulsion was quickly introduced into the homogenizer from the agitator, and vigorously stirred again, being sheared at high velocity between the narrow valve and the seat of the homogenizer, so that each droplet of dispersed phase was broken up or homogenized to a smaller size. The homogenized emulsion was also sampled to examine its stability.

The stability of emulsion prepared with the homogenizer alone was also studied. The homogenizer first pressure was varied in the range of 130 to 490 kg/cm^2, and the second pressure was kept constant at 60 kg/cm^2.

Measurement of Emulsion Stability——The stability of an emulsion was measured with a Coulter nanosizer (Coulter Electronics Inc.), by photomicrography, and with a rheometer (type RM-1, Shimadzu Seisakusho). These methods had already been proved to be useful in our previous paper.[7)]

First, the emulsion stability was measured in terms of the degree of separation; the emulsion was left to stand in a glass tube at 20.0 °C and then the height of the separated phase appearing in the lower part of the tube was determined as a measure of the degree of separation.

Second, the emulsion stability was examined in terms of the particle diameter of emulsion droplets, using the Coulter nanosizer or photomicrography.

Finally, the emulsion stability was evaluated in terms of its rheological properties.

Results and Discussion

Effect of Agitator on Emulsification

The particle size distribution was measured under various experimental conditions. The concentration of emulsifier was varied in the range of 0.3 to 5.1%, and the revolution rate of the agitator was kept constant at 812 rpm.

The effect of agitation time on the particle diameter of the emulsion, as measured by photomicrography, is shown in Fig. 1. The particle diameter of the emulsion decreased linearly with increase in agitation time on a log-log scale. The effect of stirrer revolution rate on the particle diameter of the emulsion (measured by photomicrography) is shown in Fig. 2. The particle diameter of the emulsion also decreased linearly with increase in revolution rate on a log-log scale.

These lines yielded the following calibration equations by means of the least-squares method.

$$d_p \propto t^{-0.232} \quad (1)$$

$$d_p \propto N^{-1.25} \quad (2)$$

where d_p is particle diameter, t is agitation time, and N is revolution rate. Namely, the particle diameter was in proportion to $t^{-0.232}$ and $N^{-1.25}$. From Figs. 1 and 2, it was found

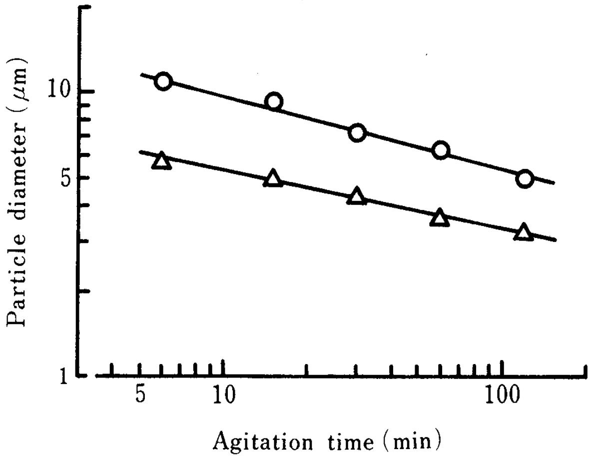

Fig. 1. Effect of Agitation Time on Particle Diameter of Emulsion Bases

Concentration of emulsifier: ○, 0.3%; △, 5.1%.
Revolution rate: 812 rpm.

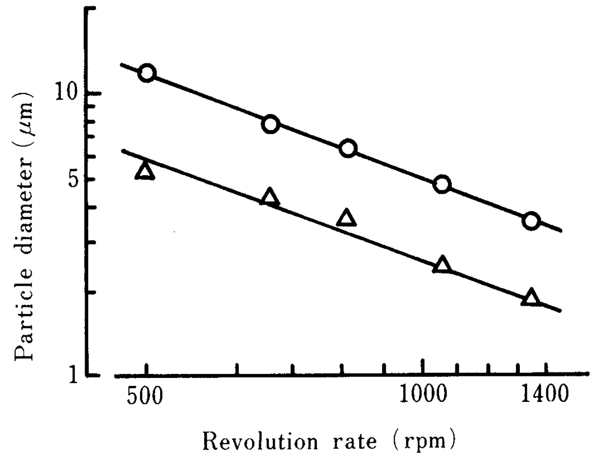

Fig. 2. Effect of Stirrer Revolution Rate on Particle Diameter of Emulsion Bases

Concentration of emulsifier: ○, 0.3%; △, 5.1%.
Agitation time: 60 min.

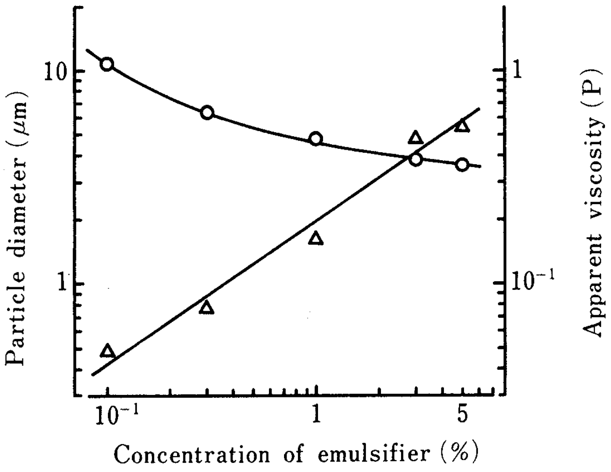

Fig. 3. Effect of Concentration of Emulsifier on Particle Diameter and/or Apparent Viscosity

○, particle diameter; △, apparent viscosity.
Revolution rate: 812 rpm.
Agitation time: 60 min.

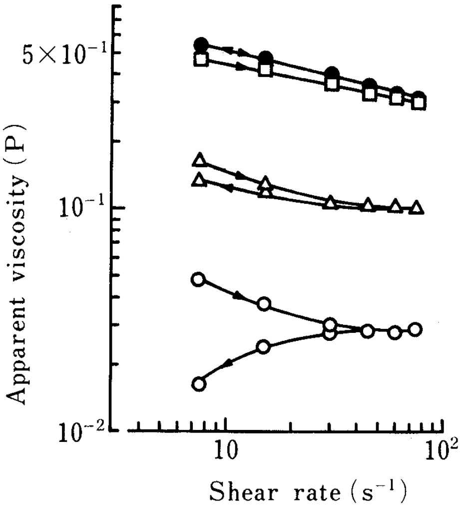

Fig. 4. Plots of Apparent Viscosity against Shear Rate for Four Different Emulsions

Concentration of emulsifier: ○, 0.1%; △, 1.0%; □, 3.0%; ●, 5.1%.
Revolution rate: 812 rpm.
Agitation time: 60 min.

that both $d(d_p)/dt$ and $d(d_p)/dN$ showed smaller values as the mean diameter of the droplets decreased. This may be because a larger shear force was necessary to break up droplets, since a droplet was still subdivided into smaller ones. These experimental results agreed fairly well with the results in our previous paper.[8]

Figure 3 shows the effect of emulsifier concentration on the paricle diameter and apparent viscosity of the emulsion base. In this measurement, the shear rate of the rheometer was kept constant at $7.5\,s^{-1}$. The agitation rate was kept constant at 812 rpm, and the agitation time was 60 min. The particle diameter of the emulsion decreased initially, and then levelled off as the concentration of emulsifier was increased. On the other hand, the viscosity of the emulsion increased linearly with increased in the concentration of emulsifier. The results in Fig. 3 suggest that emulsifier molecules may be adsorbed on the surface of droplets and thus stabilize the emulsion without coalescence. Furthermore, all excess emulsifier molecules

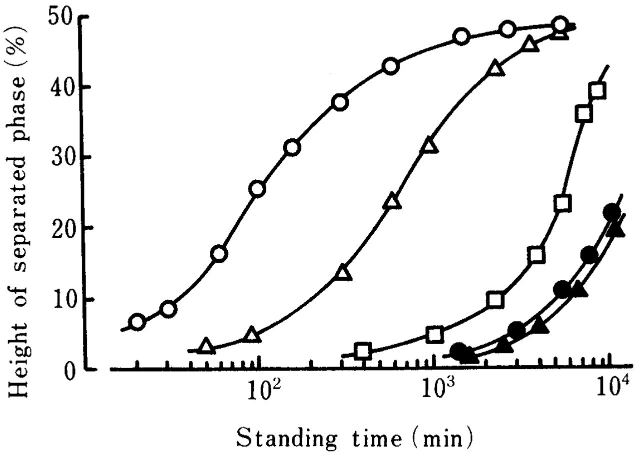

Fig. 5. Change of Height of Separated Phase of Emulsion with Standing Time

Concentration of emulsifier: ○, 0.1%; △, 0.3%; □, 1.0%; ●, 3.0%; ▲, 5.1%.
Revolution rate: 812 rpm.
Agitation time: 60 min.

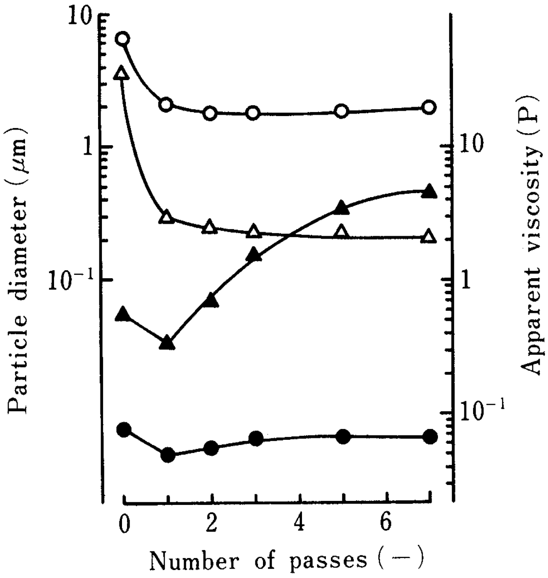

Fig. 6. Effect of Number of Passes in the Homogenizer on Particle Diameter and/or Apparent Viscosity

○, 0.3% particle diameter; ●, 0.3% apparent viscosity; △, 5.1% particle diameter; ▲, 5.1% apparent viscosity.
Pre-agitation in agitator: 812 rpm, 60 min.

associate to form micelles in the continuous phase, and these micelles immobilize continuous phase fluid. Accordingly, the emulsion viscosity may be affected by both these micelles and the flocculation of droplets.

Rheograms of emulsions prepared at four different emulsifier concentrations are shown in Fig. 4. The viscosity decreased markedly at first and then monotonously with increase in shear rate. When a low steady shear was applied to concentrated emulsion, it was often found that a steady stress did not develop instantly. This phenomenon is known as thixotropy. In particular, at low concentration of emulsifier (0.1%), the down-curve was markedly displaced to a lower position than the up-curve. This phenomenon indicates that a breakdown of emulsion having only this layer of emulsifier occurs with increasing stress (the up-curve) and that this is not reversed immediately on the down-curve, even though the stress is reduced.

The effect of emulsifier concentration on the height of the separated phase is shown in Fig. 5. At low concentration of emulsifier, the separated phase appeared rapidly after the preparation of the emulsion, and its amount gradually leveled off as the standing time increased. In general, the rate of appearance of separated phase became slower as the concentration of emulsifier increased.

Effect of Homogenizer Conditions on Emulsification

Figure 6 shows the effect of the number of passes through the homogenizer on the viscosity and the particle diameter of emulsion. The revolution rate for pre-agitation was 812 rpm, and the first and second pressures of the homogenizer were kept constant at 310 and 60 kg/cm^2, respectively.

When the concentration of emulsifier was 0.3%, the particle diameter of emulsion subjected to pre-agitation became smaller (about 1/3) at the first pass as compared to that of emulsion without pre-agitation. In the case of 5.1% emulsifier, the particle diameter of the emulsion decreased to about 1/10, but levelled off later as the number of passes was increased. These phenomena suggested that the particle diameter of the emulsion could be reduced considerably by introducing a coarse emulsion into the homogenizer at the first pass.

On the other hand, the viscosity of emulsion prepared by the homogenizer at the first pass was less than that prepared by use of the agitator alone. This temporary depression of the viscosity of emulsion in spite of the small particle diameter was considered to be caused by destruction of the inner structure of the emulsion by the homogenizer.

At a high concentration of emulsifer, the viscosity of the emulsion increased markedly with increase in the number of passes through the homogenization. This phenomenon indicates that the emulsifier molecules may be quickly adsorbed on the oil–water interface, and non-adherent molecules form many micelles in the continuous phase. Furthermore, many droplets flocculate and form a stable gel-structured emulsion. On the other hand, only a slight difference was observed between the first and fifth pass in the case of the emulsion prepared at low concentration of emulsifier. Accordingly, the use of a high concentration of emulsifiers should give emulsion type bases with excellent rheological properties when prepared with a homogenizer.

Figure 7 shows the effect of the first homogenization pressure on the particle diameter and/or the apparent viscosity of the emulsion. The agitation rate, agitation time, and the second homogenization pressure were kept constant.

The emulsion particles dispersed with the homogenizer were rapidly broken down but the effect levelled off as the first homogenization pressure was increased. The viscosity of homogenized emulsion increased slowly with increasing first homogenization pressure. In the homogenizer, a coarse emulsion enters the close-clearance area between the valve and its seat, and there is a very rapid increase in velocity, depending on the operating pressure, followed by an area of intense cavitation in the close-clearance area. Therefore, high pressure systems are most efficient in order to prepare emulsion having small particle size and high viscosity.

The changes in viscosity of the emulsion dispersed by the homogenizer with various numbers of passes are shown in Fig. 8. After the first or second pass, the viscosity of the emulsion prepared with the homogenizer decreased slowly with increase of standing time. On the other hand, no significant change was found in the apparent viscosity with emulsion-standing time.

The effect of pre-agitation on the particle diameter of the emulsion is shown in Fig. 9.

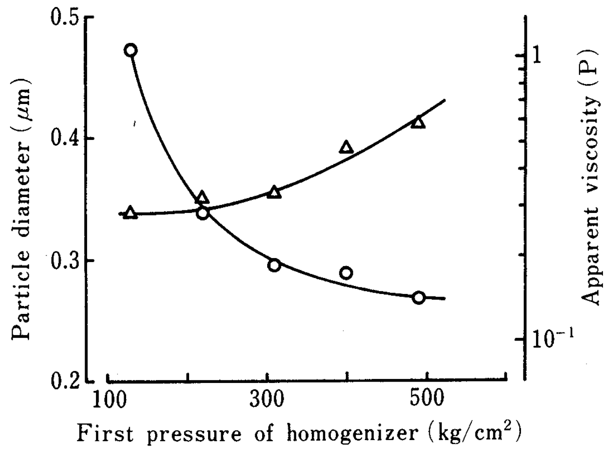

Fig. 7. Effect of First Pressure of the Homogenizer of Particle Diameter and/or Apparent Viscosity

○, particle diameter; △, apparent viscosity.
Concentration of emulsifier: 5.1%.
Pre-agitation in agitator: 812 rpm, 60 min.

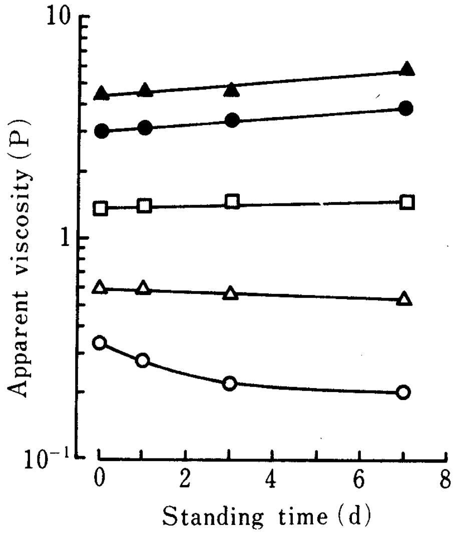

Fig. 8. Change of the Viscosity of Emulsion Bases with Standing Time

Number of passes in homogenizer: ○, once; △, twice; □, three times; ●, five times; ▲, seven times.
Concentration of emulsifier: 5.1%.
Pre-agitation in agitator: 812 rpm, 60 min.
Storage temperature: 20.0 °C.

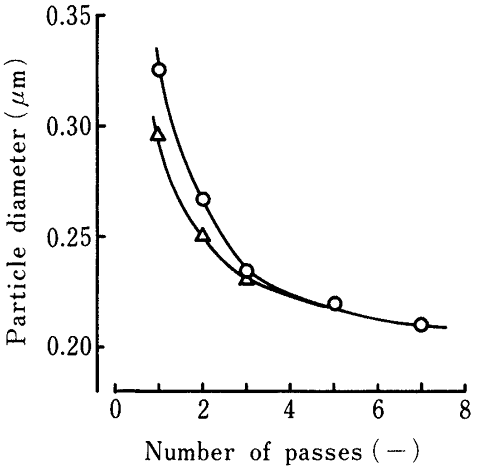

Fig. 9. Effect of Pre-agitation by Agitator of Particle Diameter

○, homogenizer; △, agitator and homogenizer.
Concentration of emulsifier: 5.1%.
Pre-agitation in agitator: 812 rpm, 60 min.
First and second pressures of homogenizer: 310 and 60 kg/cm^2.

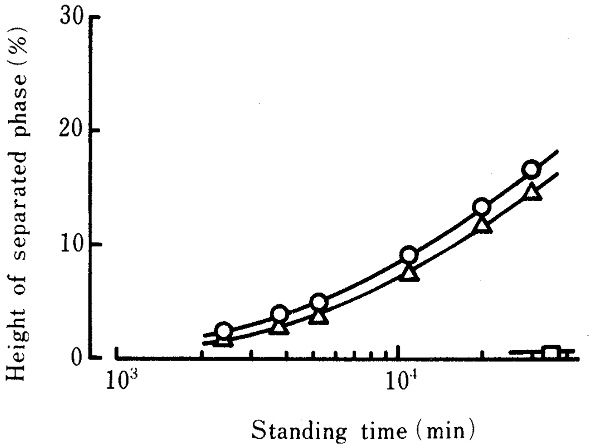

Fig. 10. Change of Height of Separated Phase of Emulsion with Standing Time

○, agitation and homogenization once (0.3%); △, agitation and homogenization five times (0.3%); □, agitation and homogenization once (5.1%).
Pre-agitation in agitator: 812 rpm, 60 min.
First and second pressures of homogenizer: 310 and 60 kg/cm^2.
Storage temperature: 20.0 °C.

The droplets were vigorously broken down in the close-clearance area between the valve and its seat, and the effect levelled off as the number of passes was increased. The emulsion prepared by the use of the agitator and the homogenizer had smaller particles than that prepared with the homogenizer alone at the first or second pass. After many homogenizations, no significant difference between the two different preparations was observed as regards the particle diameter. Therefore, exceedingly stable emulsions using 5.1% emulsifier may be achieved with the homogenizer alone.

Figure 10 shows the changes in the height of the separated phase for three different preparations of emulsions. In the case of 0.3% emulsifier, the separated phase appeared after about 2 d. The separation became slower with increasing number of passes through the homogenizer. Furthermore, no separated phase appeared at all until 14 d when the concentration of emulsifier was 5.1%.

Conclusions

With increases in the agitation time and intensity of agitation, the particle diameter of the emulsion became smaller, but a stable emulsion could not be obtained by the use of the agitator alone.

The viscosity of emulsions prepared with the homogenizer increased remarkably with increase in the number of passes in the homogenizer at a high concentration of emulsifier. However, the viscosity of the emulsion did not increase beyond expectation when the concentration of emulsifier was low.

The above-mentioned properties suggest that pre-agitation in an agitator is very useful for the preparation of emulsion products when oil and water having a low concentration of emulsifier are emulsified in a homogenizer at a single pass.

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