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# The Increasing Rate of Droplets Number on Mechanical Liquid-Liquid Dispersion

Shun'ichi Tsukiyama, Akira Takamura, and Nobuko Nakura

*College of Meiji Pharmacy*[1]

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The object of this paper is experimental discussion on dispersion rate by analogy with the theory of chemical rate processes, the calculation of rate constant $\vec{k}$ and so on.

The apparatus consists of a cylindrical vessel (150 mm$\phi$) and Rushton-type impeller (49 mm$\phi$). Water and a mixture of $n$-$C_7H_{16}$ and $CCl_4$ were used as the continuous phase and the dispersed phase, and still more Tween-20 was used as emulsifying agent. The photographs of droplets were taken by a microscopic method. Then, the particle size distribution was calculated and the following results were obtained.

1) The dispersing rate was formularized to first order of drop number as following equation.

$$\frac{dn}{d\theta} = \vec{k}(n_c - n)$$

The data of drop number in this experimental was greatly agreement with above equation.

2) The bursting ratio of drop per a revolution had an order of $10^{-3}$—$10^{-4}$, and these values gradually became small as average diameter was decreasing.

Emulsifiers have widely been employed in the physical, chemical and biological fields.[2] Many physical and chemical informations have been introduced in formation process of emulsion.[3] As various reversible factors in emulsion formation were complicated,[4] it is very difficult to theorize systematically.

Emulsion formation would be assumed to be simple two competitive process of the burst and coalesence of droplets.[5] In recent years, there are few investigations of statistical treatment for particle size distribution and specific surface area.[6,7]

In our previous papers,[8] the following experimental equation was found on the relationship between droplets' average diameter and agitation time.

$$\log d = \log C - \vec{k} \log \theta$$

The object of this paper is experimental discussion on dispersion rate by analogy with the theory of chemical rate processes, the calculation of rate constant $\vec{k}$ and so on.

## Theory

It seems that emulsification process is competition of the bursting rate and coalescing rate of droplets. Model for the deformation and breakup of drop in agitation tank was described in Fig. 1. When there was no hydrodynamic atmosphere, a drop would tend to keep a stable spherical. But, if mechanical agitation was once started, the drop was acted to the

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[1] Location: *Yatochō, Tanashi-shi, Tokyo.*
[2] H. Kitahara, *Kōgyō Zairyo*, **19**, 2 (1971).
[3] P. Sherman, *Emulsion Science*, **1969**, 1.
[4] O. Hinze, *A.I.Ch.E.J.*, **1**, 289 (1955).
[5] R. Gopal, *Rheology of Emulsions*, **1963**, 15.
[6] W.A. Rodger, V.G. Trice and J.H. Rushton, *Chem. Engng. Progress*, **52**, 515 (1956).
[7] R. Shinnar, *J. Fluid Mech.*, **10**, 259 (1961).
[8] S. Tsukiyama, H. Takahashi, I. Takashima and S. Hatano, *Yakugaku Zasshi*, **91**, 305 (1971).

strong shear stress in the agitation flow, deformed, enlarged to the flowing direction, and became a dumbell form having a concave in its center. And more, increasing the shearing force, the drop began to put out into a thread-like form, and then gradually broke up into two drops and a number of small ones.

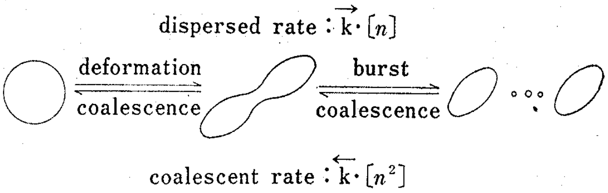

Fig. 1. Model of Burst of Fluid Drops in Shear Flow

If it is considered that the increasing rate on dispersion is the function of drop number, dispersing rate will be formularized. When coalescence may be easy to happen, it should be thought that emulsifying process is consisted of both the dispersion and coalescence direction. In this occasion, it will be possible to define a simple model that the dispersing rate proportional to first order of drop number and coalescence rate is proportional to second order of ones, so that

$$\frac{dn}{d\theta} = \vec{\mathrm{k}}\cdot n - \overleftarrow{\mathrm{k}}\cdot n^2 \qquad (1)$$

Separating the variables and integrating, Eq. (2) was obtained.

$$\ln \frac{n(n_\infty - n_0)}{n_0(n_\infty - n)} = \vec{\mathrm{k}}\cdot\theta \qquad (2)$$

This equation (2) was good agreement with the results by Gopal and the others.[9,10]

Coalescence may scarcely happened on our experimental condition because the powerful shear energy had constantly added to the dispersing liquid during agitation and it should be considered only with the dispersing direction. Drops number were rapidly increasing in the early agitation, then increasing rate of drops number became slow, and it would reach a limited value after long agitation. This result had already been mentioned and found out the following experimental formula in our previous paper; $\log d = \log C\text{-}\vec{\mathrm{k}} \log \theta$. When the dispersing rate is first order to drop number, as bellow.

$$\frac{dn}{d\theta} = \vec{\mathrm{k}}(n_c - n) \qquad (3)$$

$$\frac{1}{n}\left(\frac{dn}{d\theta}\right) = \vec{\mathrm{k}}\left(\frac{n_c}{n} - 1\right) \qquad (4)$$

$$\frac{1}{N}\left(\frac{1}{n}\right)\left(\frac{dn}{d\theta}\right) = \vec{\mathrm{k}}\left(\frac{1}{N}\right)\left(\frac{n_c}{n} - 1\right) \qquad (5)$$

Where $dn/d\theta$, $(1/n)$ $(dn/\mathrm{d}\theta)$ and $(1/N)$ $(1/n)$ $(dn/d\theta)$ are the increasing rate of drop number per second, of a friction bursted up per second and of a friction bursted up per impeller rotation. Separating the variable at Eq. (3) and integrating, Eq. (6) was obtained.

$$(n_c - n) = (n_c - n_0)e^{\vec{\mathrm{k}}\theta} \qquad (6)$$

Here $n_0$ and $n_c$ are drop number before agitation and after agitation for 10 min. If $n_0$, $n_c$ and $n$ are calculated from each experimental data, the rate constant $\vec{\mathrm{k}}$ could be determined.

## Experimental

**Equipment**——The experimental apparatus have already shown in our previous paper.[11]

**Dispersed Phase and Continuous Phase**——Distilled water, in which Tween-20 of emulsifying agent was disolved, was used as continuous phase. A mixture of $n$-$C_7H_{16}$ and $CCl_4$ prepared for 1.000 (g/cm$^3$) was used as dispersed phase. The value of cmc for Tween-20 was 0.17 (mmol/liter) and HLB was 16.0. It was

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[9] R. Gopal, *Kolloidzeitschrift*, **167**, 17 (1959).

[10] R. Gopal, *Kolloidzeitschrift*, **175**, 126 (1961).

[11] S. Tsukiyama and A. Takamura, *Yakugaku Zasshi*, **93**, 875 (1973).

commercials of Tōhō Chemical Industry. Interfacial tension with the Ring Method[11] was shown in Table I. Viscosity of liquid with Revolution Viscosity Method[12] also added in Table I. Specific viscosity $\mu_d/\mu_c$ is about 0.5 in the range of this experimental, and there is little influence to dispersion process.

Table I. Physical Properties and Experimental Condition

| | Concentration of Tween-20 % (w/w) | Revolution number and agitation time | Interfacial tension dyn/cm | Viscosity $\mu_d/\mu_c$ (−) | Specific gravity $\rho_d/\rho_c$ (−) |
|---|---|---|---|---|---|
| 1 | 0.01 | 330rpm(180min) | 20.0 | 0.5148 | 1.000 |
| 2 | | 330rpm(60min)→400rpm(120min) | | | |
| 3 | | 330rpm(60min)→530rpm(120min) | | | |
| 4 | | 330rpm(60min)→660rpm(120min) | | | |
| 5 | | 330rpm(60min)→812rpm(120min) | | | |
| 6 | 1.00 | 330rpm(180min) | 16.0 | 0.4239 | 1.000 |
| 7 | | 330rpm(60min)→400rpm(120min) | | | |
| 8 | | 330rpm(60min)→530rpm(120min) | | | |
| 9 | | 330rpm(60min)→660rpm(120min) | | | |
| 10 | | 330rpm(60min)→812rpm(120min) | | | |

**Experimental Procedures**——Agitation tank was full with 1960 ml of distilled water containing emulsifying agent. Impeller was set up in the middle of tank. Dispersed phase of 40 ml was softly put on the center of impeller as an almost globule. Concentration of dispersed phase was 2.0% (v/v) and total liquid volume was 2000 ml. Concentration of Tween-20 as emulsifying agent were respectively 0.01% and 1.00%.

To unify drop number $n_0$ in Eq. (4), pre-agitation was first carried out under the same condition at 330 rpm for 60 min. After the revolution number was rapidly changed up to the higher revolution, agitation was moreover continued for 120 min. Revolution number were 330, 400, 530, 660 and 812 rpm.

Drop size was taken by a microscopic photo method, with Nikon A.F.M. camera. Microscope was wide up 50 magnification at 330 rpm, 100 magnifications at the range of 400 rpm and 812 rpm. When revolution number was 330 rpm, dispersed liquid was sampled at 5 min intervals till 60 min. Then, it was rapidly changed up to the higher revolution number, and dispersed liquid was again sampled at settled interval till agitation time became 120 min.

Diameter of particle $d_1$ was measured by micrometer photograph which was enlarged under the same conditions. Total drop number were unified a thousand with all this experimental conditions. Mean length diameter, mean surface diameter, mean volume diameter and standard deviation were calculated by the SEIKO-S-301 computer, particle size distribution was found at intervals of five microns.

## Results

### I. Relation between Particle Size Distribution and Agitation Time

Relation of mean surface-volume diameter and agitation time were shown in Fig. 2 and Fig. 3. Concentration of emulsifying agent was 0.01% in Fig. 2, and 1.00% in Fig. 3. As soon as revolution number was changed up after the agitation to be done for 60 min at 330 rpm, mean surface-volume diameter was rapidly decreasing, and reached a limited value after 10—20 min, and diameter's diminution was scarcely found after there. That is, the decrease of average diameter is proportional to the exporrential function of the agitation time, and it may be seen that emulsifiers on mechanical agitation is completed in the range of 10—20 min.

Change of particle size distribution in the course of time was shown in Fig. 4. Concentration of emulsifying agent was 1.00%, and revolution number was 530 rpm. A peak of the distribution was gradually transfered to a small particle size with passing of agitation time. Movement of the peak became slow in proportion as agitation time passed from 10 min to 120 min.

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12) S. Tsukiyama, A. Takamura and Y. Moronuki, *Yakugaku Zasshi*, **94**, 471 (1971).

Particle size distribution was divided into three classes; first was a large group above 50 $\mu$, second was a middle group between 50 $\mu$ and 30 $\mu$, and third was small group less than 30 $\mu$. And the change of it in the course of time was shown in Fig. 5. The large group decreased with the passing of agitation time. The middle group had a maximum about 5 min, and was gradually decreasing from that point, and endly amounted to a constant value. The small group was increasing with the passing of time and came to a constant value after 20 min.

Particle size distribution at 120 min was given in Fig. 6, and it showed a straight line on a normal logarithmic scale. Accordingly, it seemed that emulsifying process would attain to the equilibrium after liquid-liquid to be agitated sufficiently.

## II. Relation between Number of Droplets and Agitation Time

Drop number per 1 $\text{cm}^3$ of dispersed phase was calculated by using the values of mean volume diameter $d_3$ and so that.

$$n = (6/\pi)(1/d_3{}^3) \qquad (7)$$

The relation between logarithmic drop number and agitation time was shown in Fig. 7 under the emulsifying agent to be 1.00%. The stage, which was agitated at 330 rpm for 60 min, was defined to zero point. As soon as revolution number was changed up to higher, drop number was rapidly increasing and became a constant value about 10 min.

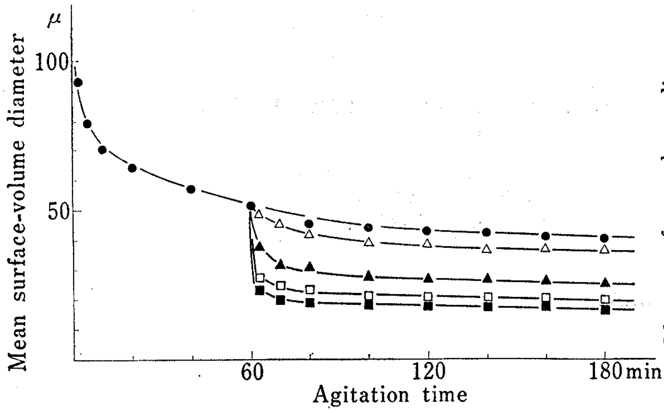

Fig. 2. Variation of Mean Surface-Volume Diameter *vs* Agitation Time

concentration of Tween-20: 0.01%
●: 330 rpm □: 660 rpm △: 400 rpm
■: 812 rpm ▲: 530 rpm

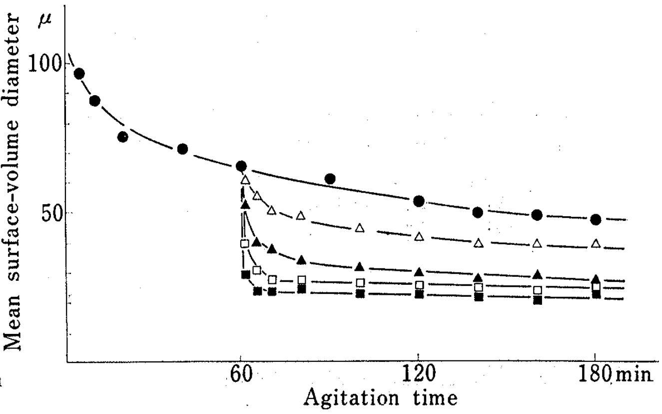

Fig. 3. Variation of Mean Surface-Volume Diameter *vs* Agitation Time

concentration of Tween-20: 1.00%
●: 330 rpm □: 660 rpm △: 400 rpm
■: 812 rpm ▲: 530 rpm

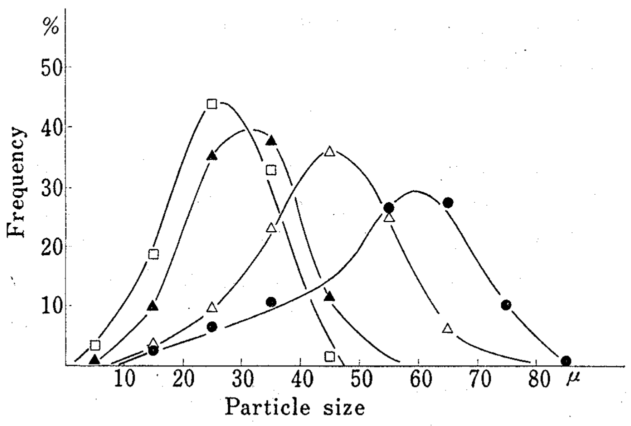

Fig. 4. Particle Size Distribution

concentration of Tween-20: 1.00%
●: 330 rpm, 60 min ▲: 530 rpm, 10 min
△: 530 rpm, 1 min □: 530 rpm, 120 min

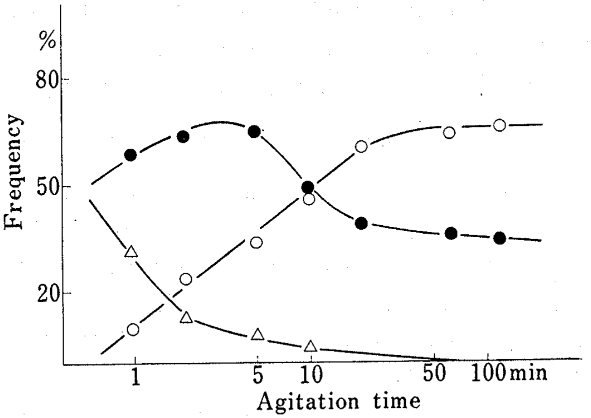

Fig. 5. Classification of Particle Size *vs* Agitation Time

concentration of Tween-20: 1.00%
revolution number : 530 rpm
○: 0—30 μ ●: 30—50 μ △: 50 μ—

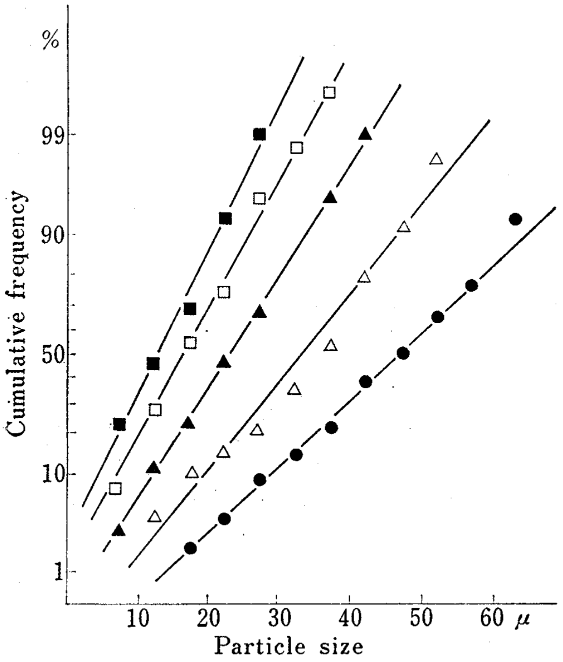

Fig. 6. Particle Size Distribution on 3 hr Agitating with Several Revolution Number

concentration of Tween-20: 1.00%
●: 330 rpm □: 660 rpm △: 400 rpm
■: 812 rpm ▲: 530 rpm

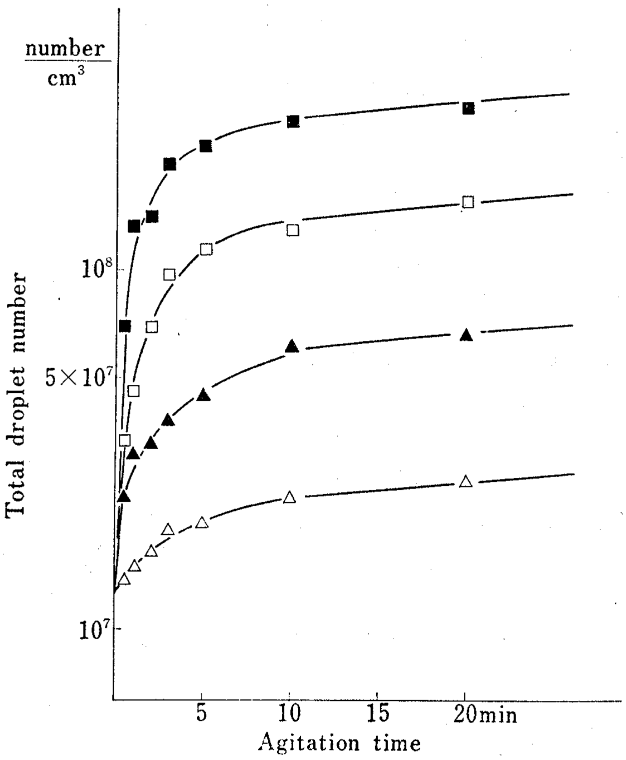

Fig. 7. Change of Total Droplet Number in the Course of Time

concentration of Tween-20: 1.00%
△: 400 rpm □: 660 rpm
▲: 530 rpm ■: 812 rpm

## Discussion

### I. The Dispersing Rate Formula

It was defined that $n_0$ and $n$ were respectively the drop number at 330 rpm for 60 min and at various revolution number for 10 min. The values of drop number at each agitation time was substituted in Eq. (6), the terms of log $[(n_c-n)/(n_c-n_0)]$ were calculated till 10 min agitation. The relation between log $[(n_c-n)/(n_c-n_0)]$ and agitation time were shown in Fig. 8. Concentration of emulsifying agent was 1.00%. Each ploted point indicated almost straight line and it increased as revolution number became higher. Therefore, it will be seen that this experimental result was in good agreement with Eq. (4). Accordingly, it will be possible to calculate the rate constant $\vec{k}$ by using the value of its grade.

$$\vec{k}(\theta_2-\theta_1) = 2.303\log[(n_c-n_1)/(n_c-n_2)] \qquad (8)$$

The values such as rate constant $\vec{k}$, half time $\tau$, mean length diameter and drop number on equilibrium state were shown in Table II. When rate constant $\vec{k}$ was determined, the bursting ratio of drop per 1 sec may be estimated from Eq. (4). The relation the dispersing rate $(1/n)$ $(dn/d\theta)$ and the logarithmic value of drop number were shown in Fig. 9. The values of dispersing rate became between $10^{-2}$ and $10^{-3}$ per second under the number to be the range of $10^7$ and $10^8$.

Still more, the relation between the bursting ratio of drop per a revolution and mean surface–volume diameter was calculated from Eq. (5) and shown in Fig. 10. The values had $10^{-3}$—$10^{-4}$ in the range of 50—20 μ of average diameter. It was found that the bursting ratio became remarkable decrease as average diameter was increasing on various revolution numbers.

## II. Surface Tension and Shear Force

On mechanical agitation process, to presume whether a drop will break up or not may be determined by the differnces of strength between surface tension of drop and shear force of agitation flow. When the shear force of agitation is more powerful than the surface tension of drop, a drop will be possible to burst and the equation will be given as following.13,14)

$$4\mu\frac{19\mu'+16}{16\mu'+16}\frac{du}{dx}>\frac{\gamma}{d} \qquad (9)$$

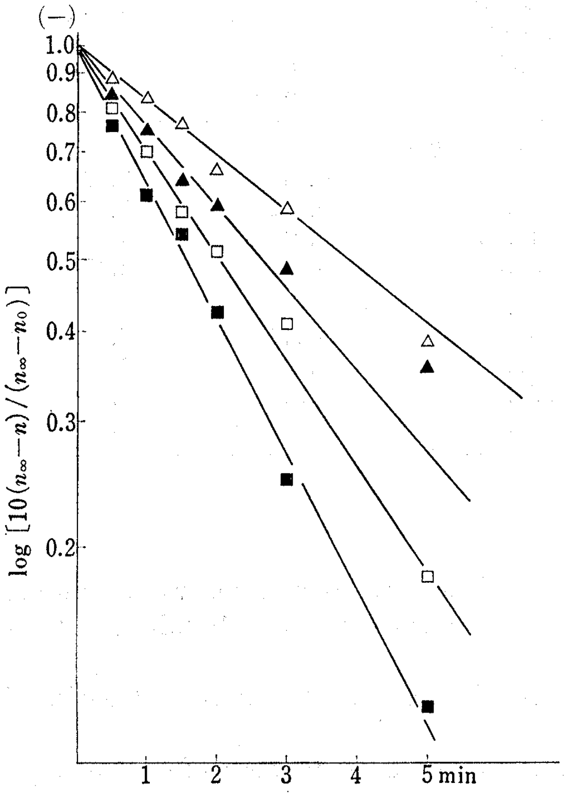

Fig. 8. Relation of $\log[10(n_\infty-n)/(n_\infty-n_0)]$ and Agitation Time

concentration of Tween-20: 1.00%
△: 400 rpm □: 660 rpm
▲: 530 rpm ■: 812 rpm

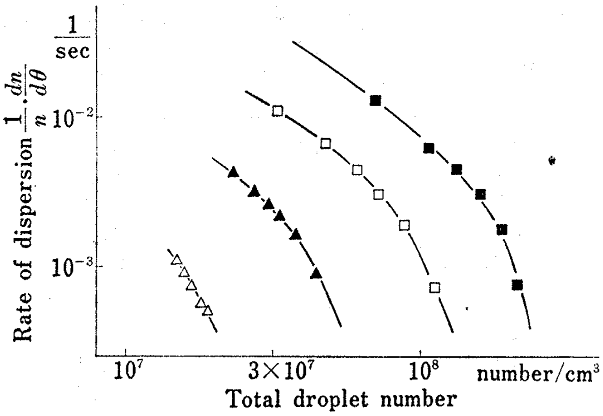

Fig. 9. Relation of Total Droplet Number and Rate of Dispersion

concentration of Tween-20: 1.00%
△: 400 rpm □: 660 rpm
▲: 530 rpm ■: 812 rpm

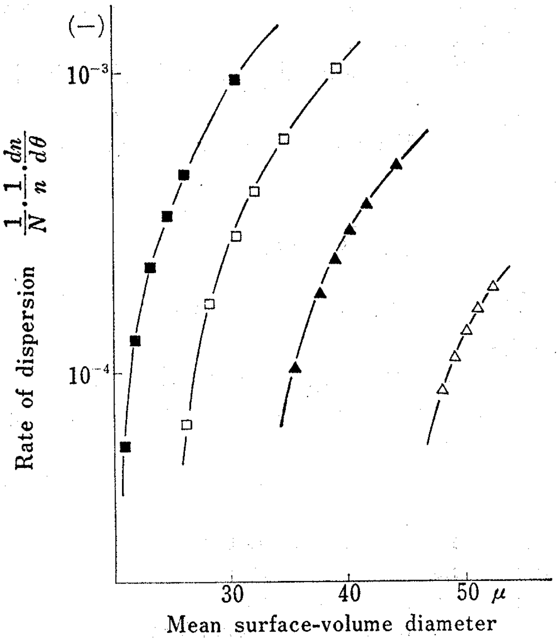

Fig. 10. Relation of Mean Surface-Volume Diameter and Rate of Dispersion

concentration of Tween-20: 1.00%
△: 400 rpm □: 660 rpm
▲: 530 rpm ■: 812 rpm

When particle size is sufficiently large, the breakup of drop will be able to happen by a little shear force. And then, it will be found a wide space of agitation tank and have a high probability. This fact is closly agreement with the initial stage on mechanical emulsion process.

When particle size becomes enough a small on mechanical agitation, the breakup of drop will be able to happen in a only greatly shear force space. The places which are affected by the intense of shear force

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13) G.I. Taylor, *Proc. Roy. Soc.*, **A146**, 501 (1932).
14) G. Mason and F.D. Rumscheidt, *J. Colloid Science*, **16**, 238 (1961).

exist only in and near impeller. So, the probability of burst would be a little. This fact will be found in the last stage on mechanical emulsion process.

As the impeller velocity becomes high speed, the more intence of shear force and the wider of space in agitation tank will be obtained. This result will be obviously procured from Fig. 10.

TABLE II. Experimental and Calculated Results

| Revolution number (rpm) | Concentration of Tween-20 % (w/w) | Mean surface volume diameter $d_\infty$ ($\mu$) | Number of particle $n_\infty$ (1/cm$^3$) | Rate constant of disperison $\overrightarrow{k}$ (1/min) | Half time $\tau$ (min) |
|---|---|---|---|---|---|
| 330 | 0.01 | 53.8 | $1.23\times10^7$ | — | — |
| 400 | | 39.3 | 3.15 | 0.118 | 7.17 |
| 530 | | 26.7 | 10.04 | 0.162 | 5.18 |
| 660 | | 24.0 | 13.82 | 0.218 | 3.86 |
| 812 | | 20.4 | 22.50 | 0.343 | 2.47 |
| 330 | 1.00 | 44.3 | 21.98 | — | — |
| 400 | | 36.4 | 39.62 | 0.117 | 7.25 |
| 530 | | 24.4 | 131.50 | 0.169 | 5.00 |
| 660 | | 19.2 | 270.00 | 0.218 | 3.86 |
| 812 | | 17.0 | 388.90 | 0.286 | 2.96 |

## Conclusion

In view of the results of this investigation, the following conclusions were obtained.

1. Mean surface-volume diameter reached a limited value at near 10 min to 20 min (Fig. 2, Fig. 3).

2. The particle size distribution in longer agitation was shown normal logarithmic (Fig. 6).

3. The dispersing rate was formularized to first order of drop number as following equation.

$$\frac{dn}{d\theta}=\overrightarrow{k}(n_c-n)$$

The data of drop number in this experimental was greatly agreement with above equation (Fig. 8).

4. The bursting ratio of drop per a revolution had an order $10^{-3}$—$10^{-4}$. And these values gradually became smaller as average diameter was decreasing (Fig. 10).

### Nomenclature

$d_1$: mean length diameter ($\mu$)
$d_2$: mean surface diameter ($\mu$)
$d_3$: mean volume diameter ($\mu$)
$d_{32}$: mean surface-volume diameter ($\mu$)
$\overrightarrow{k}$: rate constant of dispersion (min$^{-1}$)
$\overleftarrow{k}$: rate constant of coalescence (min$^{-1}\cdot$number$^{-1}$)
$n$: droplets number (number$\cdot$cm$^{-3}$)
$n_0$: droplets number befor agitation (number$\cdot$cm$^{-3}$)
$n_c$: droplets number agitation for 10 min (number$\cdot$cm$^{-3}$)
$n_\infty$: droplets number on equilibrium state (number$\cdot$cm$^{-3}$)
$N$: revolution number (sec$^{-1}$)
$\gamma$: interfacial tension (dyn$\cdot$cm$^{-1}$)
$\delta$: standard deviation of particle size (—)

$\theta$: agitation time (min)
$\mu_c$: viscosity of continuous phase (gr·cm$^{-1}$·sec$^{-1}$)
$\mu_d$: viscosity of dispersed phase (gr·cm$^{-1}$·sec$^{-1}$)
$\mu'$: specific viscosity (—)
$\rho_c$: density of continuous phase (gr·cm$^{-3}$)
$\rho_d$: density of dispersed phase (gr·cm$^{-3}$)
$\tau$: half life (min)
$du/dx$: shear velocity (sec$^{-1}$)
$dn/d\theta$: increasing rate of droplets number (number·sec$^{-1}$)

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