[Chem. Pharm. Bull. 22(11)2538—2545(1974)]

UDC 615.011.4.014

Activation Energy for the Deformation and Breakup of Droplet on Mechanical Agitation[1]

SHUN'ICHI TSUKIYAMA and AKIRA TAKAMURA

College of Meiji Pharmacy[2]

(Received March 7, 1974)

The object of this paper is to analyze the mechanism for the deformation and breakup of droplet on mechanical agitation. In this experiment, the droplets which had been subdivided to about 50 μ by pre-agitation were still more dispersed in the agitation tank. And the values of activation energy E^* and of frequency factor A were calculated.

Each average diameter of drop was calculated and the following results were obtained.

1. The value of activation energy was in the range of $5\times10^3-5\times10^4$ (erg/cm^3), when particle size was about 50 μ.
2. The value of frequency factor was in the range of $2\times10^{-3}-4\times10^{-2}$ (1/sec), when particle size was about 50 μ.

Average diameter of droplet becomes constant after long agitation time.[3] It is considered that interfacial energy is equal to agitation energy from a macroscopic point of view, or interfacial tension is equal to shear force from a microscopic point of view.[4] Therefore, it may be possible to suppose that equilibrium state will exist on liquid–liquid dispersion process. To analyze the process for the deformation and breakup of droplet, we will introduce two theories into the dispersion process. The one of these theories is the mechanic and dynamic conception for the deformation and breakup of droplet. And it had already been studied theoretically by Taylor[5] and still more experimentally by Mason.[6] The other of these theories is established with the thoughts of the Eyring's transition state,[7] and of the Arrhenius's activation energy[8] on chemical kinetics.

The object of this paper is to analyze the mechanism for the deformation and breakup of droplet on mechanical agitation by introducing these theories. In this experiment, the droplets which have been subdivided to about 50—60μ by pre-agitation are still more dispersed in the agitation tank. And the following terms are calculated on this dispersion process; rate constant $\vec{k}$, activation energy E^* and frequency factor A.

Theory

Energy Balance for the Deformation and Breakup of Droplet

Firstly, we consider the energy balance in the case that a drop is deformed and broken up in the shearing flow. A drop is continuously given a viscosity energy from a surrounding fluid, and then this energy per unit of time and volume is shown as follows.[9]

---

[1] S. Tsukiyama, A. Takamura, and N. Nakura, *Chem. Pharm. Bull.* (Tokyo), 22, 1902 (1974).

[2] Location: *Yatocho, Tanashi-shi, Tokyo.*

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

[4] Presented at the 34th Annual Meeting of Chemical Engineering Society of Japan, Tokyo, April, 1969.

[5] I. Taylor, *Proc. R. Soc.*, **A 146**, 501 (1932).

[6] F.D. Rumscheidt and S.G. Mason, *J. Colloid Sci.*, **16**, 238 (1961).

[7] H. Eyring, "The Theory of Rate Process," McGram-Hill Book Company, New York, 1941, p. 1.

[8] S. Arrhenius, *Z. Physic. Chem.*, **4**, 226 (1839).

[9] T. Nakagawa, "Lheorogy (Iwanami Zensyo)," Iwanami Shoten, Tokyo, 1969, p. 70.

$$\frac{dE_c}{d\theta} = \mu_c \cdot G_c^2 \tag{1}$$

Otherwise, a viscosity energy consumed at an inside of drop is shown as same.

$$\frac{dE_d}{d\theta} = -\mu_d \cdot G_d^2 \tag{2}$$

If a slipping loss of drop surface is neglected, the viscosity energy is accumulated as an interfacial energy, that is, a potential energy.

$$\frac{dE_c}{d\theta} - \frac{dE_d}{d\theta} = \gamma \cdot \frac{dS}{d\theta} \tag{3}$$

Therefore,

$$\mu_c G_c^2 - \mu_d G_d^2 = \gamma \cdot \frac{dS}{d\theta} \tag{4}$$

And it has already known from many experimental data in the past that a shearing velosity was proportional to an impeller velocity.[10]

$$\mu G^2 \propto u^2 \tag{5}$$

Rate of Increasing of Interfacial Area

As the powerful shear energy is constantly added to the dispersed liquid during agitation, coalescence may scarcely happened on our experimental condition and so we consider only the direction of dispersion. In this case, specific interfacial area is rapidly increasing in the early agitation, and the rate of increasing of interfacial area becomes slow, and then it would reach a limited value after a long agitation. This result has been already mentioned and found out the following experimental equation in our first report;[11] $\log d = \log c - \vec{k} \log \theta$. And still more the following formula has been obtained in our eigth report;[12] $dn/d\theta = \vec{k}\,(n_c - n)$. Here, c is the mean length diameter after agitation time to be 1 hr, and n is a number of drop per 1 g of dispersed phase. From these studies, the equation for the rate of increasing of interfacial area is shown as follows.

$$\frac{dS}{d\theta} = \vec{k}(S_c - S) \tag{6}$$

Here, S_c is a specific interfacial area at 20 min. Separating the variable and integrating, Eq. (7) is obtained.

$$(S_c - S) = (S_c - S_0) \exp(-\vec{k} \cdot \theta) \tag{7}$$

Substituting each interfacial area S_0, S_c or S into Eq. (7), rate constant $\vec{k}$ is possible to be calculated.

Mode for Deformation of Droplet

Dispersing process on immisible liquid-liquid phases is very complicated. Even the breakup mechanism of droplet in agitation tank is considered as many different patterns[13] under the differences of conditions between a particle size and an agitation intensity. For the subdivision of small size particle, not a direct cutting action of impeller but an action of

---

[10] K. Takeda, *Kagaku Kogaku*, **30**, 554 (1966).

[11] S. Tsukiyama, H. Takahashi, I. Takashima, and S. Hatano, *Yakugaku Zasshi*, **91**, 305 (1971).

[12] S. Tsukiyama and A. Takamura, *Chem. Pharm. Bull.* (Tokyo), **22**, 1902 (1974).

[13] O. Hinze, *A. I. Ch. E. Journal*, **1**, 289 (1955).

shearing stress[14] produced near the impeller will be the most effective factor. The breakup mechanism of drop is assumed as next pattern[15]; that is, a drop is exchanged into a long cylindrical thread by the shearing stress near the impeller and it finally bursts into two drops. Here, dispersion process is pressumed as a model by introducing the Eyring's theory and it is illustrated in Fig. 1. A stable sphere drop is enlarged to the direction of agitation flow, it passes through the transition state, and it finally breaks up into two or more drops. At the transition state of dispersion, an interfacial tension is equal to a shearing stress, and then the deformation of drop is stopped for a few brief moment. On this place, it is considered that there is no stress of deformation to be based on the viscosity of dispersed phase. This equilibrium is broken at a next moment, and then it will return to an initial state (I) or will proceed in the direction to (III).

Activation Energy for the Deformation of Droplet

Relation between rate constant k and activation energy E^{**} is explained by using Arrhenius's Low on thermodynamics.[8] If rate constants of chemical reaction are determined at the two different revolution number, activation energy E^{**} can be calculated.

$$E^{**} = 2.303\left(\frac{\log k_2 - \log k_1}{1/RT_1 - 1/RT_2}\right) \tag{8}$$

Transposing an atmosphere RT on chemical reaction into an atmosphere αu^2 on dispersion process,

$$RT \equiv \alpha\cdot u^2 \tag{9}$$

the activation energy E^* concerned with the deformation and breakup of drop is represented as follows in the narrow range of revolution number.

$$\begin{aligned} E^* &= 2.303\alpha \lim_{u_2\to u_1}\left(\frac{\log \vec{k}_2 - \log \vec{k}_1}{1/u_1^2 - 1/u_2^2}\right) \\ &= 2.303\alpha f'(k) \end{aligned} \tag{10}$$

And we define as this equation is the formula of activation energy on dispersion process.

Determination of the Value of α

The droplet is subdivided into a limited size ones after a long agitation time, and the rate of increasing of interfacial area $dS/d\theta$ becomes zero at that place from Eq. (6). And it is considered that a specific interfacial energy of dispersion phase per unit of time is equal to an agitation energy of continuous phase after a long agitation time.

$$E_{S_\infty} = E_{A_\infty} \tag{11}$$

where,

$$E_{S_\infty} = \gamma\cdot S_\infty, \quad E_{A_\infty} = \alpha_\infty\cdot u^2 \tag{12}$$

And the relationship between interfacial energy and agitation energy at optional agitation time is written as follows,

$$E_A = E_S \tag{13}$$

where,

$$E_S = \gamma\cdot S, \quad E_A = \alpha\cdot u^2 \tag{14}$$

From Eq. (11) and Eq. (13), α is

$$\alpha = \alpha_\infty(S/S_\infty) \tag{15}$$

---

14) I. Takashima and M. Mochizuki, *Chem. Eng. Japan*, **4**, 69 (1971).

15) W. Bartok and S.G. Mason, *J. Colloid Sci.*, **14**, 13 (1959).

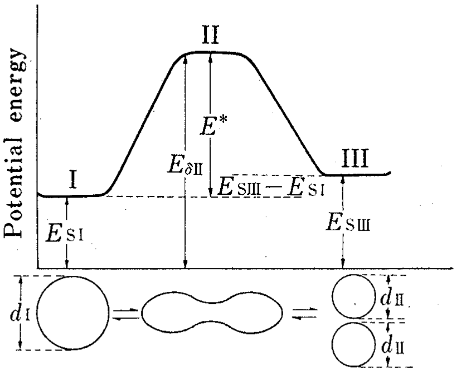
If the values of α_∞, S and S_∞ are calculated, α can be determined and moreover activation energy is obtained from Eq. (10).

Experimental

Agitation apparatus has been already shown in previous paper.[16] Furthermore, continuous phase, dispersed phase and emulsifying agent[17] has been already explained in previous paper,[18] too.

To unify interfacial area S_0 in Eq. (6), pre-agitation is first carried out under the same condition at 330 rpm for 60 min. And then, the revolution number is rapidly changed up to high ones, and moreover agitation is continued for 120 min. Revolution number are 330, 400, 530, 660 and 812 rpm respectively.

Experimental conditions are shown in Table I. Droplets are examined by microscopic photograph method.[11] Average diameter, standard deviation and particle size distribution are calculated by the SEIKO-S-301 computer.



The deformation process of drop

Fig. 1. Model for the Deformation and Breakup of Drop in the Transition State

E_{SI}: potential energy below burst
E_{SII}: potential energy beyond burst
E^*: potential energy in the activated state
$E_{SIII}-E_{SI}$: difference of potential energy between after and before burst

TABLE I. Physical Properties and Experimental Condition

	Revolution number (rpm)	Concentration of Tween-20 %(w/w)	Interfacial tension (dyn/cm)	Specific viscosity μ_d/μ_c (−)	Specific gravity ρ_d/ρ_c (−)	Sampling time (min)
1	330	0.01	20.0	0.5148	1.000	0.5, 1, 1.5, 2, 3, 5, 10, 20, 40, 60, 90, 120
2	400					
3	530					
4	660					
5	812					
6	330	1.00	16.0	0.4239	1.000	0.5, 1, 1.5, 2, 3, 5, 10, 20, 40, 60, 90, 120
7	400					
8	530					
9	660					
10	812					

Results

Change of Particle Size Distribution in the Course of Agitation Time

The relationship between particle size distribution and agitation time is shown in Fig. 2. The particle size distribution shows one peak, and then it moves to the direction of small size according as an agitation time passes.

The particle size distribution after a long agitation time is shown in Fig. 3. It shows normal distribution. And then an average diameter becomes a small ones as revolusion number is high.

---

16) S. Tsukiyama, A. Takamura, and Y. Moronuki, *Yakugaku Zasshi*, **94**, 471 (1974).
17) Tween-20 (Commerical of Toho Chemical Industry).
18) S. Tsukiyama, A. Takamura, Y. Wakamatsu, and I. Takashima, *Yakugaku Zasshi*, **93**, 191 (1973).

Rate of Increase of Interfacial Area

Change of interfacial area in the course of agitation time is shown in Fig. 4 and Fig. 5. The interfacial area attains to a limit value between 10 and 20 min. The values of average diameter and of interfacial area are given in Table II. To determine the rate constant $\vec{k}$ by using Eq. (6), the relation of $\log[(S_c-S)/(S_c-S_0)]$ and agitation time θ is shown in Fig. 6. As it shows almost a straight line, it may be possible that the rate constant $\vec{k}$ is calculated from the slope of graph. The values of rate constant $\vec{k}$ on each revolution number are given in Table III.

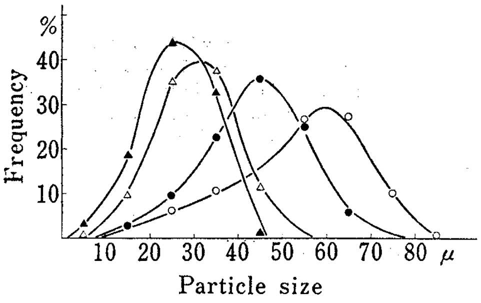


Fig. 2. Particle Size Distribution

concentration of Tween-20 1.000%
○: 330 rpm, 60 min ●: 530 rpm, 10 min
△: 530 rpm, 1 min ▲: 530 rpm, 120 min

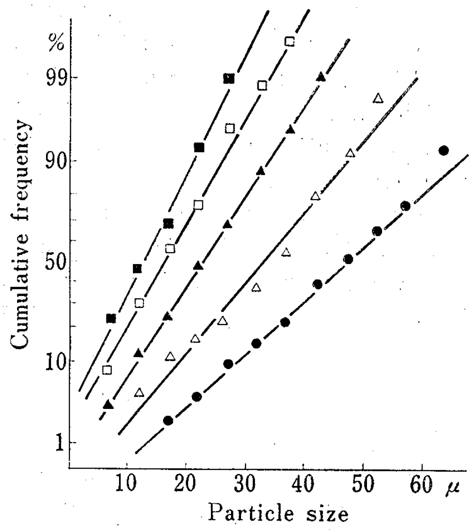


Fig. 3. Particle Size Distribution on 3 hr Agitating at Various Revolution Number

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

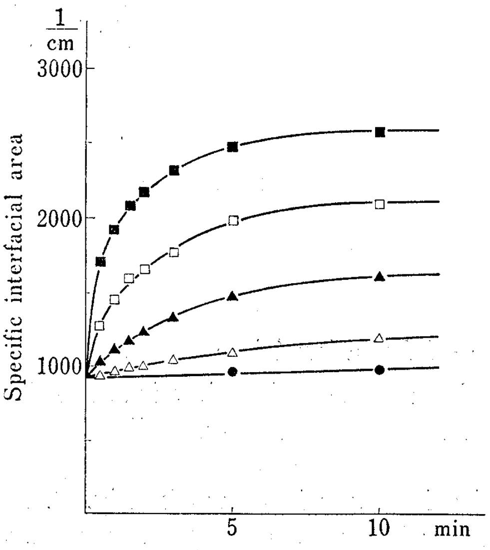


Fig. 4. Change of Specific Interfacial Area in the Course of Time

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

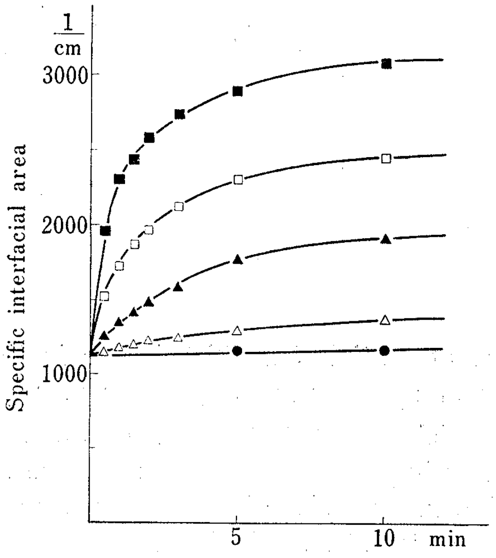


Fig. 5. Change of Specific Interfacial Area in the Course of Time

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

Table II. Experimental and Calculated Results

Revolution number (rpm)	Concentration of Tween-20 %(w/w)	u (cm/sec)	u^2 (cm^2/sec^2)	d_0 (μ)	d_∞ (μ)	S_0 (1/cm)	S_∞ (1/cm)	E_{s0} (erg/cm^3)	$E_{s\infty}$ (erg/cm^3)
330	0.01	86	0.75×10^4	66.3	53.8	9.04×10^2	1.11×10^3	1.80×10^4	2.23×10^4
400		103	1.06		39.3		1.53		3.05
530		136	1.84		26.7		2.25		4.49
660		169	2.85		24.0		2.50		5.00
812		208	4.06		20.4		2.94		5.88
330	1.00	86	0.75×10^4	53.1	44.3	1.13×10^3	1.35×10^3	1.80×10^4	2.17×10^4
400		103	1.06		36.4		1.65		2.63
530		136	1.84		24.4		2.46		3.94
660		169	2.85		19.2		3.12		5.00
812		208	4.06		17.0		3.53		5.66

Table III. Activation Energy and Frequency Factor

Revolution number (rpm)	α_∞	α	$\vec{k}$ (1/min)	$f'(k)$ (−)	E^* (erg/cm^3)	A (1/sec)	A' (−)
330	3.00	2.79	0.100	0.932	5.24×10^{-3}	2.15×10^{-3}	0.39×10^3
400	2.88	1.70	0.126	2.111	8.27	7.63	1.15
530	2.44	0.98	0.216	6.35	14.3	10.4	1.18
660	1.75	0.63	0.349	15.3	22.2	14.6	1.46
812	1.44	0.44	0.600	30.8	31.4	40.0	2.96
330	2.92	2.44	0.103	0.932	5.25×10^3	2.15×10^{-3}	0.39×10^{-3}
400	2.48	1.70	0.135	2.11	8.25	7.63	1.15
530	2.14	0.98	0.318	6.35	14.4	10.4	1.18
660	1.75	0.63	0.343	15.3	22.3	14.6	1.46
812	1.39	0.45	0.572	30.8	31.6	40.0	2.96

Relationship between Interfacial Energy and Agitation Energy

The relation of interfacial energyand agitation energy after an agitation time to be done for 120 min are shown in Fig. 7. The value of α_∞ can be obtained from Eq. (11) and moreover the value of α from Eq. (13). These calculated values are given in Table III.

Activation Energy and Frequency Factor for the Breakup of Drop

To obtain an activation energy, the interrelation of log $\vec{k}$ and $(1/\alpha u^2)$ are shown in Fig. 8. It does not show a straight line. The slope $f'(\vec{k})$ has a large value with the increasing of impeller's velocity. The value of $f'(\vec{k})$ at each revolution number is obtained from Fig. 8, and activation energy is calculated from Eq. (10). So, the value of activa tion energy becomes in the range of 5×10^3 and 3×10^4 (erg/cm^3), and it shows a large value with the increasing of revolution number. The values are

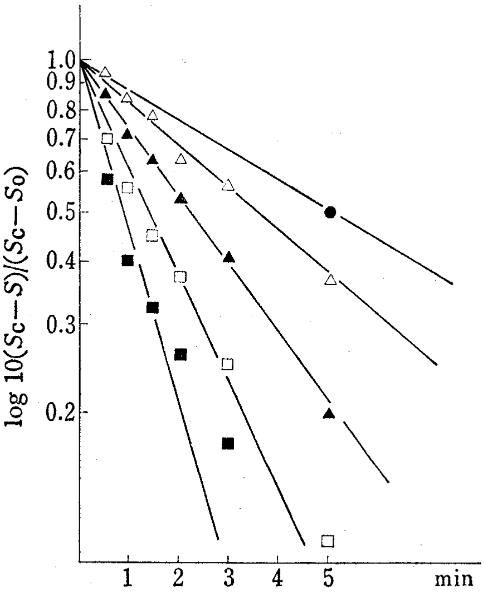


Fig. 6. Relation between log[10(S_C-S)/(S_C-S_0)] and Agitation Time

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

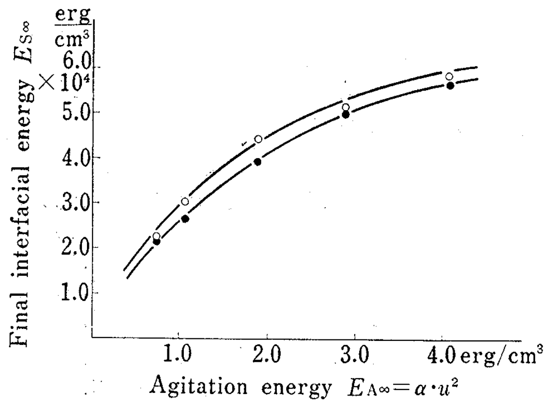


Fig. 7. Relationship between Final Interfacial Energy and Agitation Energy

●: concentration of Tween-20: 1.00%
○: concentration of Tween-20: 0.01%

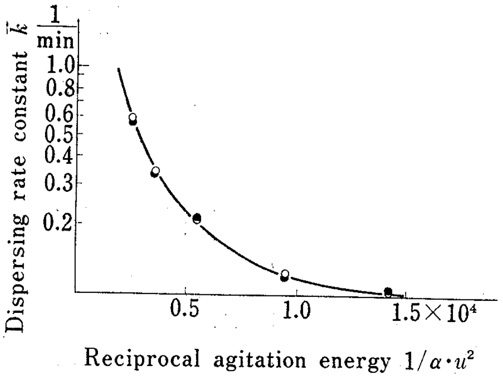


Fig. 8. Dispersing Rate Constant *v.s.* Reciprocal Agitation Energy

●: concentration of Tween-20: 1.00%
○: concentration of Tween-20: 0.01%

almost the same when the concentrations of emulsifying agent are 0.01 and 1.00% (w/w).

Subsequently, a tangent line is drawn at each section of the curve in Fig. 8, and then a frequency factor A is calculated from a point of intersection between the tangent line and the ordinate. The values of frequency factor A become in the range of 2×10^{-3} and 4×10^{-2} (1/sec), have a large with the increasing of revolution number.

Discussion

The theoretical bases that Eyring's theory is possible to be applied are as follows. The first is considered that the dispersion process is governed by the only giving and receiving of energy. And the second is considered that the transition state may be in existance on dispersion process. Then, if the deformed drop reaches here, it will proceed either positive or negative direction. And still more dispersion phenomena is considered of the isovolumetric change because there is no volume change on the deformation and breakup of drop. Dispersion is caused by the burst of individual drop, but the changing property in consequence is the increase of interfacial area only, and then it can be considered that there is no effect of other things on this dispersion. Accordingly, the interfacial energy is thought of the potential energy in dispersion system.

On the other hand, the most important factor of the atmosphere around a drop will be not the thermodynamic conditions of temperature and pressure, but the intensity of shear stress to effect a drop. If the flow pattern are the same in hydrodynamics, it is thought that this shear stress is proportional to velocity of flow. It has been already studied that this flow was yielded by impeller of agitator, and the velocity of flow was proportional to impeller's ones from many previous experimental data.[19] It will be proper that the most of energy given to a drop is the kinetic energy yielded by the tip of impeller. The flow in the tank may be the turbulent flow because it is sufficiently agitated with a impeller. But, it is considered that the shearing flow exists in the agitated flow from the microscopic point of view. Therefore, the mechanism for the deformation and breakup of drop, which have already investigated by Mason and his assistants, will be able to apply to the agitation system, and it seems that transition state exists on the deformation and breakup of drop, too.

At any rate, the activation energy E^* for the deformation and breakup of drop can be calculated. This result will be a valuable guide in the case of the calculation of shear velocity and the study for the deformation and breakup mechanism of droplet.

---

19) W. Bartok and S.G. Mason, *J. Colloid Sci.*, 12, 243 (1957).

Conclusion

In view of the results of this investigation, the following conclusion are obtained.

1. In equilibrium state, it is considered that interfacial energy is equal to agitation energy.
2. It seems to be quite all right to introduce Eyring's theory concerned with the transition state into the deformation and breakup process of a droplet.
3. The relation between rate constant $\vec{k}$ and activation energy E^* are shown as follows.

$$E^* = 2.303\alpha \lim_{u_2 \to u_1} \left(\frac{\log \vec{k}_2 - \log \vec{k}_1}{1/u_1{}^2 - 1/u_2{}^2} \right)$$

4. The value of activation energy is in the range of $5 \times 10^3 - 5 \times 10^4$ (erg/cm^3), when particle size is about 50 μ.
5. The value of frequency factor is the range of $2 \times 10^{-3} - 4 \times 10^{-2}$ (1/sec), when particle size is about 50 μ.

Nomenclature

A	;	frequency factor (1/sec)
d_0, d_{I}, d_{II}, d_∞	;	mean surface volume diameter (μ)
E_{A}, $E_{\mathrm{A}\infty}$	;	agitation energy (erg/cm^3)
E_{S}, $E_{\mathrm{S}\infty}$, E_{SI}, E_{SII}	;	specific interfacial energy (erg/cm^3)
E^*, E^{**}	;	activation energy (erg/cm^3)
$f'(k)$	;	a gradient, Fig. (8)
G, G_{c}, G_{d}	;	shear velocity (1/sec)
k, k_1, k_2	;	rate constant of chemical reaction (1/min)
$\vec{k}_1$, $\vec{k}_2$	;	rate constant of dispersion (1/min)
R	;	gas constant (cal/mole·deg)
S, S_{c}, S_0, S_∞	;	specific interfacial area (1/cm)
T, T_1, T_2	;	absolute temperature (°K)
u, u_1, u_2	;	impleller velocity (cm/sec)
α, α_∞	;	a coefficient, Eq. (13) (g/cm^3)
γ	;	interfacial tension (dyn/cm)
δ	;	standard deviation (−)
θ	;	agitation time (min)
ρ_{c}, ρ_{d}	;	specific gravity (g/cm^3)
μ, μ_{c}, μ_{d}	;	viscosity (poise)
$dE_{\mathrm{c}}/d\theta$, $dE_{\mathrm{d}}/d\theta$	;	energy of viscosity per minute (erg/cm^3·sec)
$ds/d\theta$	;	rate of increase of interfacial area (1/cm·sec)

Acknowledgement We grateful acknowledge to Dr. M. Koishi, associate professor Science University of Tokyo and Mr. H. Hidaka, lecturer of Meisei University for suggesting this problem and for stimulating interest in it.