[Chem. Pharm. Bull. 22(11)2565—2572(1974)]

UDC 615.011.4.014

Model for the Deformation of Droplet in Agitation Flow[1]

SHUN'ICHI TSUKIYAMA and AKIRA TAKAMURA

College of Meiji Pharmacy[2]

(Received April 1, 1974)

The object of this paper is to make several models for the deformation and breakup of droplet by introducing the transition state theory into the process of liquid-liquid dispersion on mechanical agitation.

On this experiment, the droplets which had been grown to about 50—60 μ pre-agitation were still more dispersed in the agitation tank, continuously. And a value of maximum shearing velosity was calculated and then a shape of deformed drop was presumed.

The droplets were taken by a microscopic photograph method. Then, average diameter was mesured and the following results were obtained.

1. When the mode of deformed drop is assumed as an ellipsoid, it will be considered that a drop about 50 μ will burst into two drops at the range of 330 and 530 rpm.

2. A value of maximum shearing velosity in the agitation tank becomes 3.8×10^{3} (1/sec) at 330 rpm and 2.50×10^{4} (1/sec) at 812 rpm, respectively.

The deformation and breakup of droplets in both shear and plane hyperbolic flows have been already theorized by Taylor[3] and proved by Mason.[4,5] It has however been executed in the idealized flow pattern and the particle diameter had a large value in the range of 1 mm and 330 μ.

It is very technically difficult to observe directly the phenomena for the deformation of droplets on mechanical agitation. One of these difficulty causes by the next reason; that is, both the real value of shearing velocity and the flow pattern in agitator can not be solved, because the flow in agitation tank is the complete turbulent flow and very complexity.[6] The other is due to that it is impossible to take directly a photograph for the shape of deformed drop in the turbulent flow.

Here, we introduce the Eyring's transition state theory[7] on the kinetic rate reaction into the process of liquid-liquid dispersion, and calculate the value of activation energy for the breakup of drop. And moreover, we presume how to the deformation and breakup of drop from these data.

On this experiment, the droplets which had been grown to about 50—60 μ by pre-agitation were still more dispersed in the agitation tank, continuously.

The object of this paper is to make several models for the deformation and breakup of droplet by introducing the transition state theory into process of liquid-liquid dispersion on mechanical agitation, and the next terms are calculated; activation energy, maximum shearing velocity and so on.

Theory

Activation Energy and Specific Interfacial Energy

If it will be considered that the activation energy is equal to the increase of specific interfacial energy, equation is given by;

1) S. Tsukiyama and A. Takamura, *Chem. Pharm. Bull.* (Tokyo), **22**, 2545 (1974).
2) Location: *Yatocho, Tanashi-shi, Tokyo.*
3) I. Taylor, *Proc. R. Soc.*, **A 146**, 501 (1932).
4) G. Mason and F.D. Rumscheidt, *J. Colloid. Sci.*, **16**, 238 (1961).
5) G. Mason and W. Bartok, *J. Colloid. Sci.*, **14**, 13 (1959).
6) I. Takashima and M. Mochizuki, *Chem. Eng.*, **4**, 69 (1971).
7) H. Eyring, "The Theory of Rate Process," McGraw-Hill Book Company, New York, 1941, p. 1.

$$E^* = \gamma \cdot S^* \qquad (1)$$

And, when a drop will be put into the transition state as described in Fig. 1, the following equation is obtained.

$$E_1 + E^* = \gamma(S+S^*) \qquad (2)$$

If a ratio of the potential energy between below burst and at transition state will be calculated, as follows.

$$\frac{E_1+E^*}{E_1} = \frac{S+S^*}{S} \qquad (3)$$

Eq. (3) means that a ratio of potential energy is equal to that of interfacial area. Therefore, if ratio of potential energy will be obtained, it will be possible to presume the deformed shape of drop at the transition state on mechanical agitation.

Mode for the Deformation of a Drop

The deformation and breakup of drop in shearing flow, which have already been studied by Taylor,[3] Mason[4] and the others,[8] will be considered with two pattern as shown in Fig. 2. One is that a drop is elongated to the direction of shearing flow and forms an ellipsoid having an angle of 45° to the axis of the flow. Then a center of drop is gradually constricted and at last it bursts into two drops.[3,4] The other is that a drop is enlarged to the direction of the flow having constriction of n parts and it bursts into n number of drops as shown in Pattern II of Fig. 2.

If we consider that I_A in Fig. 2 is one ellipsoid, I_B or II_B is two and II_C is n number, an analysis for the deformation mechanism of drop will be able to be evolved. When the length of ellipsoid is a and the breadth is b, the values of both a volume and an interfacial area of drop at the transition state are given by Eq. (4) and Eq. (5), respectively.

$$V = \frac{4\pi ab^2}{3} \qquad (4)$$

$$S + S^* = 2\pi\left[b^2 + \frac{a^2b}{\sqrt{a^2-b^2}} \cos^{-1}\left(\frac{b}{a}\right)\right] \qquad (5)$$

Equations for a volume and an interfacial area at each pattern are given in Table I.

Deformation to One Ellipsoid

As the deformation from a sphere to an ellipsoid is isovolumetric change, equation concerned with a volume is given by,

$$V = \frac{4\pi r^3}{3} = \frac{4a_1b_1^2}{3} \qquad (6)$$

And, a ratio of interfacial area between the state bellow burst and the state at transition is written by,

$$\frac{S+S^{**}}{S} = \frac{2\pi\left[b^2 + \dfrac{a_1^2b_1}{\sqrt{a_1^2-b_1^2}} \cos^{-1}\left(\dfrac{a_1}{b_1}\right)\right]}{4\pi r^2} \qquad (7)$$

It we put,

$$b_1 = k_1a_1 \qquad 1>k_1>0 \qquad (8)$$

Here, if a radius of sphere bellow is put unit then Eq. (8) is substituted into Eq. (6), a_1 is rewritten by next,

$$a_1 = k_1^{-2/3} \qquad (9)$$

8) O. Hinze, *A. I. Ch. E. Journal*, 1, 289 (1955).

Moreover, substituting Eq. (8) into Eq. (7), the following equation is obtained,

$$\frac{S+S^{**}}{S} = \frac{k_1^{-1/3}}{2}\left(k_1+\frac{1}{\sqrt{1-k_1^2}}\cos^{-1}k_1\right) \tag{10}$$

From Eq. (10), a ratio of interfacial area can be dealt with the function of k_1, which equals to a ratio between length and breadth of ellipsoid.

Deformation to Two Ellipsoids

As the deformation from a sphere to two ellipsoids is isovolumetric change too, equation is given by

$$V = \frac{4\pi r^3}{3} = 2\times\frac{4\pi a_2 b_2^2}{3} \tag{11}$$

And a ratio of interfacial area between the state bellow burst and the state at transition is written by,

$$\frac{S+S^*}{S} = 2\times\frac{2\pi\left[b_2^2+\frac{a_2^2 b_2}{\sqrt{a_2^2-b_2^2}}\cos^{-1}\left(\frac{b_2}{a_2}\right)\right]}{4\pi r^2} \tag{12}$$

If we put;

$$b_2 = k_2\cdot a_2 \qquad 1>k_2>0 \tag{13}$$

Here, if a radius of sphere bellow burst is put unit and then Eq. (13) is substituted into Eq. (11), a_1 is rewritten by next;

$$a_2 = 2^{-1/3}\cdot k^{2/3} \tag{14}$$

Moreover, substituting Eq. (13) into Eq. (12), the following equation is obtained,

$$\frac{S+S^*}{S} = 0.63\,k_2^{-1/3}\left[k_2+\frac{1}{\sqrt{1-k_2^2}}\cos^{-1}(k_2)\right] \tag{15}$$

The values calculated from Eq. (15) are shown in Fig. 3.

Deformation to n Number of Ellipsoids

As the deformation from a sphere to n number ellipsoids is isovolumetric change too, equation is given by,

$$V = \frac{4\pi r^3}{3} = n\times\frac{4\pi a_3 b_3^2}{3} \tag{16}$$

As the state of II_C is thought of the transition state, a ratio of interfacial area is represented as follows.

$$\frac{S+S^*}{S} = \frac{2n\pi\left[b^2+\frac{a_3^2 b_3}{\sqrt{a_3^2-b_3^3}}\cos^{-1}\left(\frac{b_3}{a_3}\right)\right]}{4\pi r^2} \tag{17}$$

If a drop is sufficiently enlarged until a ratio of length and breadth of ellipsoid is three to one,[3] equation is shown as next;

$$a_3 = 3\cdot b_3 \tag{18}$$

Here, if radius of sphere bellow burst sets to unit and then Eq. (18) is substituted into Eq. (16), n is rewritten by,

$$n = 9/a_3^3 \tag{19}$$

Moreover, substituting Eq. (19) into Eq. (17), the following equation is obtained,

$$\frac{S+S^*}{S} = \frac{2.459}{a_3} \tag{20}$$

From Eq. (20), if a ratio of interfacial area is fixed, a length a_3 is calculated, and still more both breadth b_3 and number of drops are determined.

Presumption of Maximum Shearing Velocity on Mechanical Agitation

In our previous studies, the values of average diameter in equilibrium have been already required. When an average diameter reaches a limit value, a drop is deformed until the state of B in Fig. 2, but the deformation of drop will return to the initial state of ones.

$$\frac{4\pi r_\infty^3}{3} = \frac{4\pi a_\infty b_\infty^2}{3} \tag{21}$$

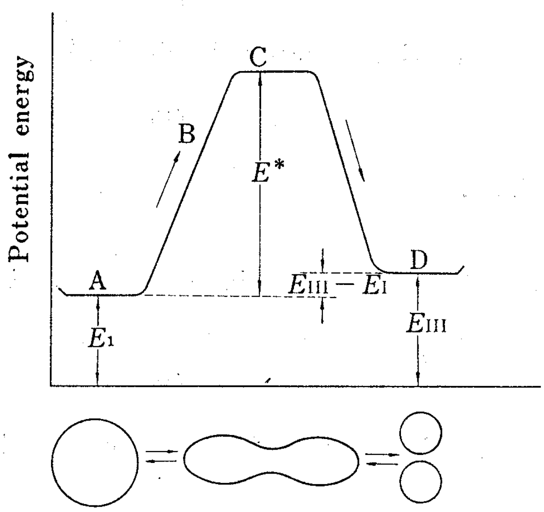
From the theoretical analyses by Taylor[3] and the others,[4,8] dynamic balance equation at the transition state is given by,

$$\mu_c f(\mu')\frac{du}{dx} = \frac{\gamma}{2b_\infty} \tag{22}$$

Here, $f(\mu')$ is the correction efficiency concerned with the viscosity, and it is represented as follows.

$$f(\mu') = \frac{19\mu'+16}{16\mu'+16} \qquad (1.0 \leqq f(\mu') \leqq 1.2) \tag{23}$$

Therefore, if a breadth of ellipsoid at the transition state is calculated, it will be possible to estimate a maximum shear force $\mu_c(du/dx)$ or a maximum shearing velocity du/dx on mechanical agitation.



Droplet's dispersing pass

Fig. 1. Model for the Breakup of Drop in the Activated State

E_I: potential energy below breakup
E_{III}: potential energy beyond breakup
E^*: potential energy at activated state
$E_{III}-E_I$: difference of potential energy between beyond and below

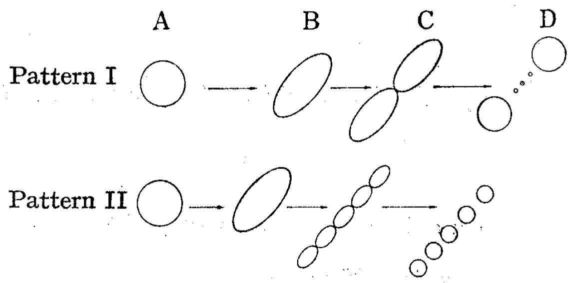


Fig. 2. Typical of Deformation and Burst of Drops in Shear Flow

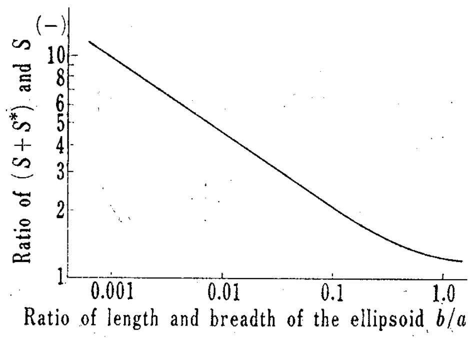


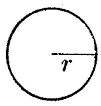
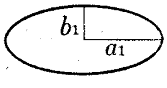
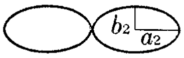
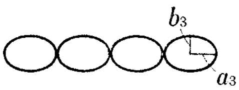
Fig. 3. Ratio of Surface Area *v.s.* Ratio of Length and Breadth of the Ellipsoid Pattern Ic

Experimental

Agitation apparatus consisted of a cylindrical vessel (150 mmϕ) with 4 baffles and an impeller of standard turbine type (49 mmϕ).[9]

9) S. Tsukiyama, A. Takamura, and Y. Moronuki, *Yakugaku Zasshi*, **94**, 471 (1974).

TABLE I. Volume and Surface Area in Each Model

Pattern	Figure	Volume	Surface area
I_A, II_A		$4\pi r^3/3$	$4\pi r_2$
I_B, II_B		$4\pi a_1 b_1^2/3$	$2\pi[b_1^2+(a_1^2 b_1/\sqrt{a_1^2-b_1^2})\cos^{-1}(b_1/a_1)]$
I_C		$8\pi a_2 b_2^2/3$	$4\pi[b_2^2+(a_2^2 b_2/\sqrt{a_2^2-b_2^2})\cos^{-1}(b_2/a_2)]$
II_C		$4n\pi a_3 b_3^2/3$	$2n\pi[b_3^2+(a_3^2 b_3/\sqrt{a_3^2-b_3^2})\cos^{-1}(b_3/a_3)]$

Distilled water, in which Tween-20[10)] was dissolved, was used as continuous phase. And a mixture of n-C_7H_{16} and CCl_4, of which density was adjusted to 1.000 (g/cm^3), was used as dispersed phase. Concentration of emulsifying agent were both 0.01 and 1.00% (w/w). Revolution number were 330, 400, 530, 660, and 812 rpm respectively.

Droplets' size were taken by a microscopic photograph method.[11)] Average diameter, standard deviation and particle size distribution were calculated by the SEIKO-S-301 computer.

Results

Calculation of Specific Interfacial Energy

As the values of potential energy both bellow breakup and at transition state have been already required in our recent paper, a value of $(S+S^*)/S$ at Eq. (3) is calculated and shown in Table II. It is found that these values show 1.29 times at 330 rpm and 2.74 times at 812 rpm respectively.

Presumption for the Deformed Shape of Droplets

Firstly, a deformed shape is presumed when a droplet is devided into two ones. A value of k_2 having a value of $(S+S^*)/S$ is required from Fig. 3. And the values of a_2 and b_2 are calculated by substituting a value of k_2 into Eq. (13) and Eq. (14). Moreover, if it is assumed that k_1 equals to k_2, the values of a_1 and b_1 are calculated by using Eq. (8) and Eq. (9), and these values are given in Table II. It is shown in Fig. 4 that a mode for the deformed process of droplet at Pattern I in Fig. 2. From this calculated data, it seems that a drop is considerably enlarged at 812 rpm. From this calculated data, it seems that a drop is considerably enlarged at 812 rpm.

Secondly, when a drop is change into many ones as illustrated in Pattern II of Fig. 2, various data are calculated. A value of a_3 is required from Eq. (20), those of b_3 and n are calculated from Eq. (18) and Eq. (19), and then these values are given in Table II, too. On this calculated data, we see that a drop is divided to 3.5 numbers at 530 rpm and 12.5 numbers at 812 rpm. A value of n is rounded off and the deformed shape of drop at the transition state is illustrated in Fig. 5. But, a value of n at 330 rpm puts to 2.

10) Tween-20 (Commerical of Tōhō Chemical Industry). S. Tsukiyama, A. Takamura, Y. Wakamatsu, and I. Takashima, *Yakugaku Zasshi*, **93**, 191 (1973).
11) S. Tsukiyama, H. Takahashi, I. Takashima, and S. Hatana, *Yakugaku Zasshi*, **91**, 305 (1971).

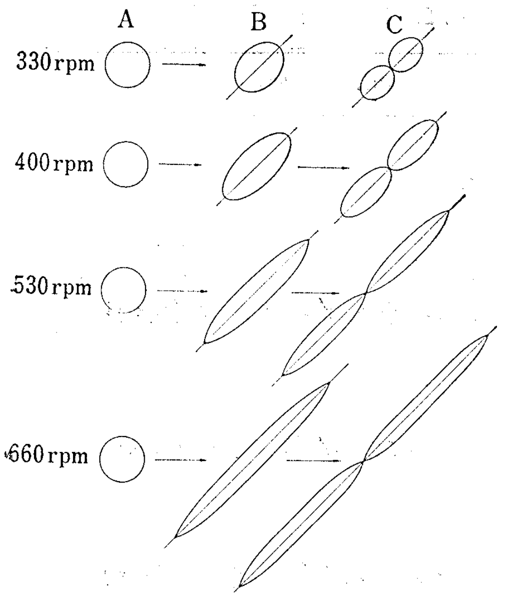


Fig. 4. Calculated Deformation and Burst of Drops in Shear Flow (Pattern I)

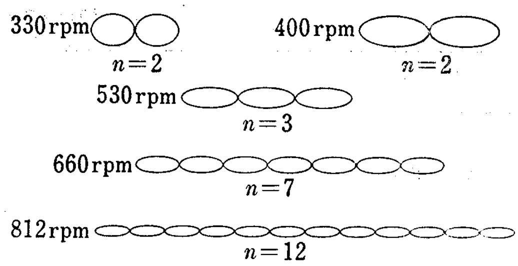


Fig. 5. Calculated Deformation and Burst of Drops in Shear Flow (Pattern II)

mean length diameter: about 50 μ

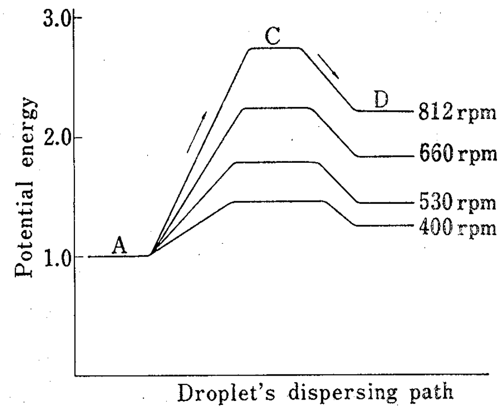


Fig. 6. Calculated Model of the Breakup of Drop in the Activated State

A: state below breakup
C: state of activation
D: state beyond breakup

Calculation of a Maximum Shearing Velocity on Mechanical Agitation

Substituting the values such as μ_C, γ and b_∞ into Eq. (22), those of a maximum shear force $\mu_C(du/dx)$ and a maximum shearing velocity du/dx on mechanical agitation are calculated, and then these value are given in Table III. A value of shearing velocity becomes in the range from 10^3 to 10^5 order, and this value is remarkably more than that of previous data[6] which have been required from the analysis for the photograph method of flow pattern in agitation tank.

Table II. Experimental and Calculated Results

	E^* (erg/cm^3)	$(S+S^*)/S$ (−)	a_1 (−)	b_1 (−)	k_2 (−)	a_2 (−)	b_2 (−)	a_3 (−)	b_3 (−)	n (−)	T-20 %(w/w)
330 rpm	5.25×10^3	1.29	1.203	0.912	0.758	0.955	0.724	1.91	0.635	1.30	0.01
400	8.27	1.46	2.033	0.701	0.345	1.613	0.556	1.68	0.561	1.88	
530	14.34	1.79	3.311	0.550	0.166	2.625	0.436	1.37	0.458	3.47	
660	22.24	2.23	5.091	0.443	0.0871	4.039	0.352	1.10	0.368	6.71	
812	31.43	2.74	7.368	0.368	0.0500	5.848	0.293	0.897	0.299	12.45	
330 rpm	5.25×10^3	1.29	1.203	0.912	0.758	0.955	0.724	1.91	0.635	1.30	1.00
400	8.27	1.46	2.033	0.701	0.345	1.613	0.556	1.68	0.561	1.88	
530	14.34	1.79	3.311	0.550	0.166	2.625	0.436	1.37	0.458	3.47	
660	22.24	2.23	5.091	0.443	0.0871	4.039	0.352	1.10	0.368	6.71	
812	31.43	2.74	7.368	0.368	0.0500	5.848	0.293	0.897	0.299	12.45	

Discussion

Firstly, we will discuss the propriety of the mode for the deformation of drop. The deformed shapes at 330, 400 and 530 rpm are good agreement with Mason's observations and this mode will be thought to be existed. But, the enlargement of drop at 660 or 812 rpm is

TABLE III. Experimental and Calculated Results

	μc (gr/cm-sec)	μ' (−)	$f(\mu')$ (−)	γ (dyn/cm)	d_∞ (μ)	$2b_\infty$ (μ)	f (dyn/cm^2)	du/dx (1/sec)	T-20 %(w/w)
330 rpm	1.000	0.5148	1.064	20.0	53.8	49.1	4.07×10^3	3.83×10^3	0.01
400					39.3	27.5	7.27	6.84	
530					26.7	14.7	13.6	12.8	
660					24.0	10.6	18.9	17.7	
812					20.4	7.51	26.6	25.0	
330 rpm	1.000	0.4239	1.056	16.0	44.3	40.4	3.96×10^3	3.72×10^3	1.00
400					36.4	25.5	6.27	5.94	
530					24.4	13.4	11.9	11.3	
660					19.2	8.51	18.8	17.8	
812					17.0	6.26	25.6	24.2	

unstable and this mode will be impossible to be existed. Preferably, on the condition of high revolution number, it will be thought that a drop is instantly divided into many number of drops and then a dispersed drop is gradually broken up into two ones. All activation energy on the high revolution number is not used as the increasing of interfacial energy, but a part of this energy is consumed as the plastic and elastic strain of deformation or the heat of friction.[12] It has been already described by Mason that there were several various mechanisms for the deformation and breakup of droplet dependent on a ratio of the viscosity between dispersed phase and continuous phase. But, an effect of viscosity can not be almost considered on this experiment, because the range of a ratio of viscosity is nearly consant from 0.4 to 0.5. When it is assumed that the shapes of deformed drop are Pattern I of Fig. 2 at 330—530 rpm and Pattern II at 660—812 rpm respectively, the mode for the deformed drop on mechanical agitation will be thought to be property. The synthetic mode of deformed drop are illustrated in Fig. 6.

Secondly, we will deal with both a shear force and a shearing velocity. It is noted that the treatment of this force must be due to the only means of statistical analysis, because the flow pattern is very complexity and still more the changes of both time and space are greatly wide. From a microscopic point of view. It is thought that the equilibrium at the transition state is the dynamic balance, that is, it is treated with the relation between surface tension and shear force. Therefore, there is a foundation that this mode can be established by introducing the theory of Taylor and Mason. At last, a maximum shearing velocity, which have been almost impossible to measure till today, can be calculated on mechanical agitation. It will be thought that this result will be a variable guide for many dispersion operation.

Conclusion

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

1. Activation energy for the deformation of droplet is consumed as the increasing of specific interfacial energy.

2. When the mode of deformed drop is assumed as an ellipsoid, it will be considered that a drop about 50 μ will burst into two drops at the range of 330 and 530 rpm.

3. When a drop size is about 50 μ, it will be thought that a drop will burst into many drops from six to twenty.

4. From a dynamic point of view, the transition state on dispersion process is considered with the balance between an interfacial tension of drop and a shear force of agitation flow.

12) W. Monk, *J. Appl. Phys.*, 23, 288 (1952).

5. A maximum shearing velocity in the agitation tank becomes 3.83×10^3 (1/sec) at 330 rpm and 2.50×10^4 (1/sec) at 812 rpm respectively.

Nomenclature

a	:	length of ellipsoid (μ)
b	:	breadth of ellipsoid (μ)
d	:	mean length diameter at long agitation time (μ)
E	:	specific interfacial energy (erg/cm³)
E^*	:	activation energy (erg/cm³)
f	:	shearing force (dyn/cm²)
k	:	ratio between length and breadth (—)
n	:	number of droplet (—)
r	:	radius of droplet (μ)
S	:	specific interfacial area (1/cm)
V	:	volume of droplet (μ³)
γ	:	interfacial tension (dyn/cm)
μ	:	viscosity (poise)
μ'	:	ratio of viscosity (—)
$f(\mu')$	:	correction efficiency of viscosity (—)
du/dx	:	shearing velocity

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