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Studies on an Emulsion Formation by Flow Jet Mixer. A Simple Method for Determination of the Average Droplet Size of Coarse Emulsion from Measurements of Turbidity[1]

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The object of this paper is to be determined the calculation equation between the turbidity and the specific interfacial area of dispersion for emulsion systems.

The emulsion was prepared by the Flow Jet Mixer. The droplet size distributions were concurrently measured by the turbidimetric method and the microscopic method. Distilled water and mixtures of n-C_7H_{16} and CCl_4 were used as continuous phase and the dispersed phase, respectively, in absence of emulsion agent.

Hence, the following results were obtained.

1) The relationship between the turbidity, I, and the concentration of dispersed phase, C, were as following.

$$\log I = 1.321 \log C + \beta$$

where β was the intercept.

2) As same as presented in term 1), the relation between the specific interfacial area, S, and the concentration of dispersed phase were represented by,

$$S = -2046 \log C + \beta'$$

Consequently, where β' was the intercept.

3) Combining above two equations, the next calibration equation could be established for these emulsion systems.

$$S = 4505 + \log (I^{1590}/C^{2046})$$

Keywords——emulsion; Flow Jet Mixer; interfacial area; mean length diameter; microphotographic method; particle size distribution; revolution number; Turbidimeter

If the turbidity of an emulsion of large spherical particles is independent of the wavelength of light, the turbidity measured by the turbidimeter can be represented as functions of both the average diameter of the particle size distribution and the concentration of dispersed phase.[3] The determinations of the average particle size with the light scattering or the turbidimetry methods have been studied by Garrent[4] or Bagchi.[5]

Now, the calibration equation between the turbidity and the average diameter of droplets, or the concentration of dispersed phase, would be desired to be experimentally established for emulsion systems. The present investigation, therefore, was directed toward developing a method of determining the average droplet size of emulsion systems directly from the turbidity measurement. Since the droplet sizes of the emulsion prepared in absence of emulsifying agent are usually much larger than the wavelength of light, these emulsion systems are in the domain of geometrical optics.[6] The extinction is primary due to refraction and reflection of

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3) M.J. Akers and J.L. Lach, *J. Pharm. Sci.*, **65**, 216 (1976).

4) *a)* E.R. Garrett, *J. Pharm. Sci.*, **54**, 1557 (1965); *b)* N.E. Doyd, *J. Colloid Sci.*, **14**, 441 (1959).

5) P. Bagchi and R.D. Vold, *J. Colloid and Interface Sci.*, **53**, 194 (1975).

6) M. Kerker, "The Scattering of Light and Other Electromagnetic Radiation," Academic Press, New York, 1969.

light incident on the droplets, and diffraction of light passing near the edges of the droplets. For such system, it has been shown that the turbidity is proportional to the specific interfacial area of emulsion.[7] If the specific interfacial area of emulsion can be determined easily and quickly from measurement of the turbidity without requiring knowledge of particle size distribution, it will be considered to be conventional method for the investigation of physical or chemical properties of emulsion.

Now, both the measurements of turbidity and the particle size distribution with a microscopic method[8] are concurrently undertaken for each sample of emulsion. Accordingly, the calibration equation concerned with the relation between the turbidity and the specific interfacial area can be discussed, in this paper, for the coarse emulsion systems yield yielded by the Flow Jet Mixer.

Experimental

Equipments——A sketch of the apparatus employed is shown in Fig. 1. The mixer can feed the emulsion to the successive process continuously and quantitatively. In preparation of emulsion, water and oil can be emulsified into a stable, extremely fine emulsion, oil-in-water or water-in-oil type within a few seconds. The detailed descriptions of Flow Jet Mixer had already shown in previous paper.[9]

The turbidimeter used was PT-201 type of Nihon Seimitsu Kōgaku Co., Ltd.[1] Since the turbidimeter adopts the integration sphere method of electrophotometer, the turbidity could exactly be measured. In this turbidimetry, the term, turbidity (I) was determined as the ratio of diffused and transmitted light quantity (I_D) and the parallel transmitted light quantity (I_P).

$$I = \frac{I_D}{I_P} \times 100 \qquad (1)$$

Here, the value of turbidity of emulsion could be measured comparing with the ones of distilled water only. The values of turbidities were measured in the range of 0—500 ppm of concentration of emulsion. The cell containing an emulsion was inserted into the cell inlet and covered with a tight fitting black box to eliminate stray light, and the turbidities were measured. The specimen box was surrounded and circulated with the air controlled at $20.0 \pm 0.1°$ by the thermostat in order to keep the temperature of emulsion sample at 20.0°. The changes of turbidities and temperatures with time were simultaneously recorded, respectively, on the

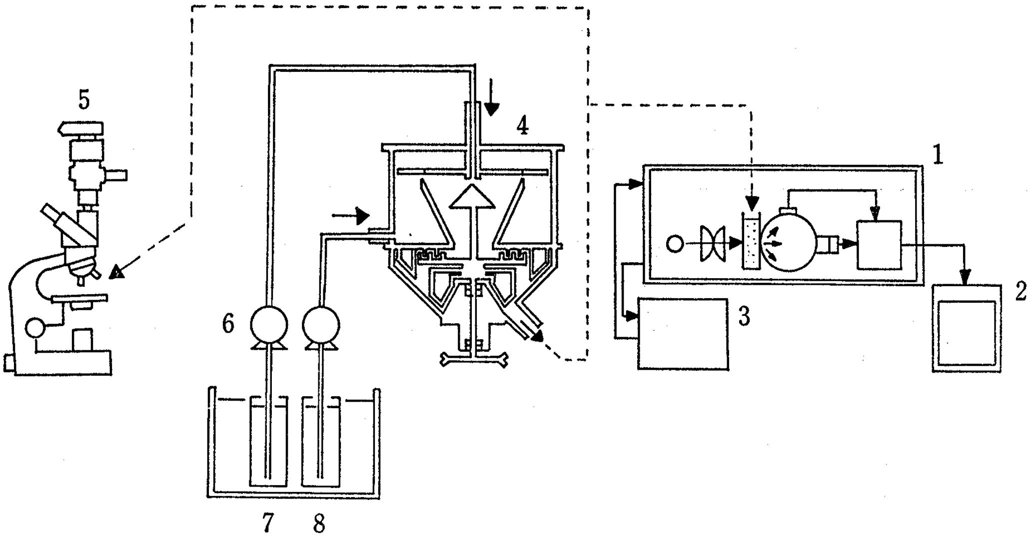

Fig. 1. Apparatus

1: turbidimeter, 2: recorder, 3: thermostat, 4: Flow Jet Mixer, 5: microscope, 6: pump, 7: vessel(dispersed phase), 8: vessel(continuous phase).

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[7] a) G. Mie, *Ann. Physik.*, **25**, 377 (1908); b) M. Bornstein, J.L. Lach, and B.J. Munden, *J. Pharm. Sci.*, **54**, 1653 (1968).

[8] T. Kubo, S. Tsukiyama, A. Takamura, and I. Takashima, *Yakugaku Zasshi*, **91**, 518 (1971).

[9] A. Takamura, S. Noro, and M. Koishi, *Chem. Pharm. Bull.* (Tokyo), **25**, 1113 (1977).

B-281H type recorder of Rika Electro Co., Ltd. The camera used in this study was AFM type of Nikon with equipped a microscope.

Experimental Procedures——In order to determine the average droplet size of coarse emulsion, the both methods of turbidimetry and microscope were used in this work.

Firstly, the experimental procedures of turbidimetric method were explained. As the turbidity of emulsion sample could not be measured under the condition of high concentration in the range of 3.55 to 27.50 % (v/v), the emulsion was sufficiently diluted by a distilled water. The emulsion yielded by the Flow Jet Mixer was poured into a beaker. In succession, some definite volume of emulsion was quickly sampled with a pipette and diluted with 200 ml of distilled water. Here, no-coalescence of droplets were confirmed under a microscope. After 5 ml of the emulsion was added in the cell, it was inserted into the cell inlet. Readings of turbidity were taken within 2—3 min.

Each sample of emulsion was photographed with a Nikon AFM camera equipped with a microscope at the same time as the measurement of turbidity. The diameters of droplets were measured with a micrometer scale which had been photographed and enlarged under the same conditions.[10] The number of droplets measured was one thousand in all cases. The mean length diameter, the mean surface diameter, the mean volume diameter, the standard deviation, and the particle size distribution were calculated by a Seiko-S-301 Computer.[11]

Measurement of Physical Properties——Distilled water and mixtures of n-C_7H_{16} and CCl_4 were used as the continuous phase and the dispersed phase, respectively. The density of dispersed phase was adjusted so as to be the same as that of the continuous phase[12] (1.000 gr/cm^3). The emulsifying agent was not used in this study. The total concentration of dispersed phase used in this study were 3.55 and 27.50% (v/v). Interfacial tensions were measured by the ring method (Kyōwa Chemical Co., Ltd.).[13] And the viscosities of the liquid were measured by a rotating viscometer (Shibaura Electric Co., Ltd.) at $20.0\pm0.1°$.[14]

The concentration of dispersed phase, sampled volume of emulsion, concentration of dispersed phase measured by the turbidimeter, specific gravity, viscosity of emulsion, interfacial tension, and revolution number are summarized in Table I.

TABLE I. Physical and Mechanical Properties at Each Experimental Condition

	Concentration of dispersed phase C_1 %(v/v)	Sampled volume of emulsion v_1 (ml)	Concentration of dispersed phase measured by the turbidimeter %(v/v)	Specific gravity ρ_d/ρ_c (−)	Viscosity of emulsion μ_e (cp)	Interfacial tension $\lvert\gamma_d-\gamma_c\rvert$ (dyn/cm)	Revolution number N (rpm)
Emulsion A	3.55	0.5—15.0	8.85×10^{-5} —2.48×10^{-3}	1.000	1.15	48.5	1258, 1460, 1668, 2120, 2400
Emulsion B	27.50	0.5— 8.0	6.86×10^{-4} —1.06×10^{-2}	1.000	1.15	48.5	888, 1072, 1258, 1668, 2120

Results and Discussion

Relations between the Specific Interfacial Area of Emulsion and the Revolution Number

The specific interfacial area of emulsion was calculated by using the mean surface-volume diameter of droplets size,[15]

$$S=\frac{6\sum d_i^2}{\rho_d\sum d_i^3}=\frac{6}{\rho_d d_{sv}} \qquad (2)$$

where S is the specific interfacial area (cm^2/gr), ρ_d is the specific gravity of dispersed phase (gr/cm^3), and d_{sv} is the mean surface-volume diameter (cm).

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10) S. Tsukiyama, H. Takahashi, I. Takashima, and S. Hatano, *Yakugaku Zasshi*, **91**, 305 (1971).
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12) S. Tsukiyama and A. Takamura, *Shikizai Kyōkaishi*, **48**, 151 (1975).
13) S. Tsukiyama, A. Takamura, Y. Wakamatsu, and I. Takashima, *Yakugaku Zasshi*, **93**, 191 (1973).
14) S. Tsukiyama, A. Takamura, Y. Fukuda, and M. Koishi, *Bull. Chem. Soc.*, **48**, 3561 (1975).
15) K. Kubo, E. Mizuwatari, Y. Nakagawa, and S. Hayakawa, "Funtai," Maruzen, Tokyo, 1974, p. 88.

Figure 2 gives the relations between the specific interfacial area of emulsion and the revolution number of mixing disk. The concentration of dispersed phase were 3.55 and 27.50% (v/v). The ranges of revolution number were from 888 to 2400 rpm. It was found from Fig. 2 that the values of specific interfacial area have larger ones over the whole range of the revolution number for a lower concentration of the dispersed phase. Furthermore, the specific interfacial area increases noticeably with increasing the revolution number, indicating that it is greatly affected by the revolution number. The calculated values of mean length diameter, mean surface diameter, mean volume diameter, standard deviation, particle number, and specific interfacial area are summarized in Table II.

Relations between the Turbidity and the Concentration of Emulsion

After the emulsion prepared by the Flow Jet Mixer was sampled by the pipette, it was quickly diluted with 200 ml of distilled water. The net concentration of emulsion (C) was calculated from the both values of the initial stock concentration (C_1) and the sampled volume of emulsion (v).[16] The calculated concentration values (C) were in the range of 10^{-4} and 10^{-2} % (v/v).

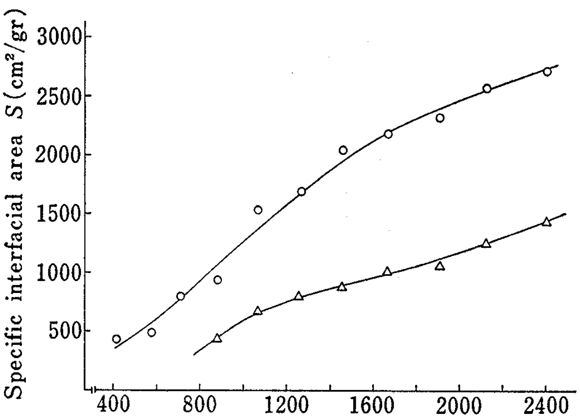

Fig. 2. Relations between Specific Interfacial Area of Emulsion and Revolution Number of Mixing Disk

○: concentration of dispersed phase 3.55 %(v/v).
△: concentration of dispersed phase 27.50 %(v/v).

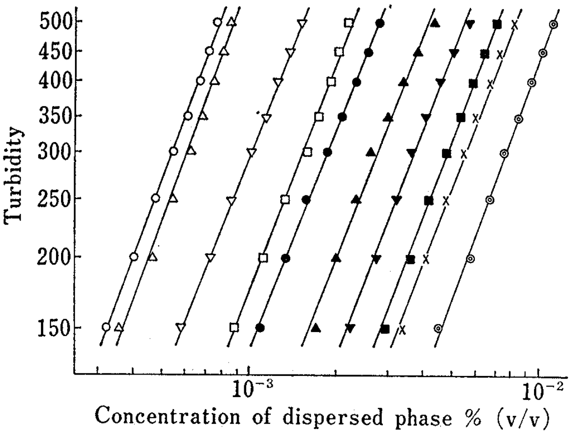

Fig. 3. Relations between Turbidity and Concentration of Dispersed Phase

○: 3.55 %, 2400 rpm; △: 3.55 %, 2120 rpm;
▽: 3.55 %, 1668 rpm; □: 3.55 %, 1460 rpm;
●: 3.55 %, 1258 rpm; ▲: 27.50 %, 2120 rpm;
▼: 27.50 %, 1668 rpm; ■: 27.50 %, 1258 rpm;
×: 27.50 %, 1072 rpm; ◎: 27.50%, 888 rpm.

Table II. Calculated Values of d_l, d_s d_v, σ, n, and S

Concentration of dispersed phase (% v/v)	Revolution number (rpm)	Mean length diameter d_l (μm)	Mean surface diameter d_s (μm)	Mean volume diameter d_v (μm)	Standard deviation σ (−)	Particle number n (1/gr)	Specific interfacial area S (cm²/gr)
3.55	2400	17.78	18.64	19.75	5.59	247.9 × 10^6	2705
	2120	18.38	19.43	20.64	6.29	217.2	2576
	1668	20.17	21.57	23.32	7.63	150.6	2200
	1460	22.09	23.71	25.36	8.60	117.1	2067
	1258	28.68	30.42	32.28	10.16	56.78	1650
27.50	2120	27.29	31.61	36.34	15.94	39.80 × 10^6	1250
	1668	32.98	38.94	44.98	20.72	20.99	1000
	1258	44.31	50.22	55.97	23.64	10.89	863
	1072	47.95	54.42	63.47	25.74	7.47	695
	888	63.80	77.66	94.10	44.28	2.29	434

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[16] $C = C_1 \times v/(200+v)$.

log-log plots of the turbidity against the concentration of dispersed phase for the ten different emulsion systems studied are shown in Fig. 3. It was found experimentally as seen in Fig. 3 that the points fitted very well on a straight line with the data of Emulsion A and Emulsion B. These lines yielded the following calibration equation by means of a least squares method

$$\log I = 1.321 \log \mathrm{C} + \beta \qquad (3)$$

where log I was the specific turbidity of emulsion and β was the intercept of Fig. 3. In addition, the values of gradient, intercept, and interrelation calculated from Fig. 3 are given in Table III for ten plotted lines. It is noteworthy that the individual value of gradients agree with the average gradient within 4.5% for the emulsion systems of sufficiently large droplet size.

TABLE III. Calculated Values from Fig. 3

Concentration of dispersed phase (% v/v)	Revolution number (rpm)	Gradient	Intercept at 10^{-3} (% v/v)	Interrelation coefficient
3.55	2400	1.360	2.837	0.999
	2120	1.364	2.768	0.995
	1668	1.272	2.470	1.000
	1460	1.319	2.234	0.998
	1258	1.257	2.137	1.000
27.50	2120	1.265	1.920	0.993
	1668	1.289	1.740	0.997
	1258	1.376	1.537	0.999
	1072	1.380	1.457	0.999
	888	1.332	1.302	0.999

Average of gradients : 1.321 ± 0.046.

Relations between the Specific Interfacial Area and the Concentration of Emulsion

The relations between specific interfacial area and concentration of emulsion are shown in Fig. 4. The specific interfacial area of emulsion are obtained from Fig. 2. The turbidities of emulsions ranged from 150 to 500. For emulsion systems, it was found experimentally, as seen in Fig. 4 that the specific interfacial area against the logarithmic concentration of dispersed phase was linear with an inversely slope. The values of gradients for five points of turbidities are calculated by a least squares method and then given in Table IV. The average of gradients was -2046 ± 20, hence, a calibration equation for these lines can be written as,

$$S = -2046 \log C + \beta' \qquad (4)$$

where β' was the intercept at Fig. 4.

Combining Eq. (2) and (3), the turbidity for emulsion systems can be represented as functions of concentration of dispersed phase and of specific interfacial area of emulsion. In this emulsion system, the calibration equation was given as following,

$$S = K + \log [I^{1590}/C^{2046}] \qquad (5)$$

where, K is the constant value. In this case, no-change of S due to adhesion, was experimentaly confirmed.

In order to determine the value of K, $[S - \log(I^{1590}/C^{2046})]$ were calculated at variable concentrations of dispersed phase and shown in Fig. 5. These plots indicated that the value of K was nearly constant ones. The average value of K was calculated from 72 points of concentration and these value showed 4505 ± 50. Hence, the following experimental equation was given for the turbidity method in this emulsion system.

$$S = 4505 + \log (I^{1590}/C^{2046}) \qquad (6)$$

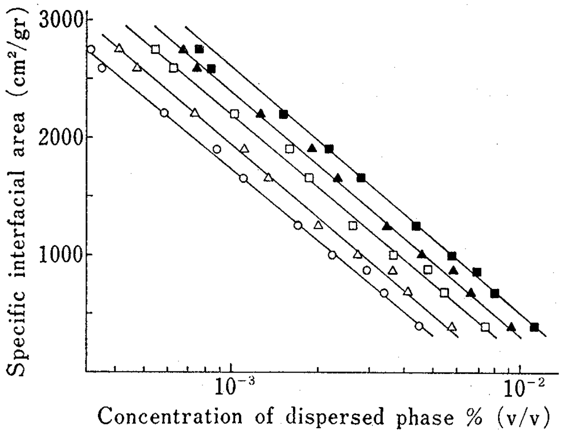

Fig. 4. Relations between Specific Interfacial Area and Concentration of Dispersed Phase

○: I=150, △: I=200, □: I=300, ▲: I=400, ■: I=500.

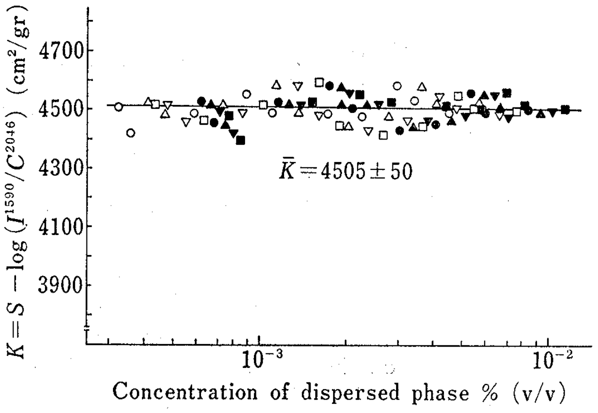

Fig. 5. Values of K *vs.* Concentration of Dispersed Phase

○: I=150, △: I=200, ▽: I=250, □: I=300, ●: I=350, ▲: I=400, ▼: I=450, ■: I=500.

TABLE IV. Calculated Values from Fig. 4

Turbidity (ppm)	Gradient	Intercept at 10^{-3} %(v/v)	Interrelation coefficient
150	-2.008×10^{3}	1.739×10^{3}	1.001
200	-2.037	1.935	1.001
250	-2.044	2.080	1.001
300	-2.062	2.208	1.000
350	-2.059	2.306	1.001
400	-2.052	2.394	1.002
450	-2.029	2.461	1.000
500	-2.074	2.602	0.990

Average of gradient: $(-2.046\pm0.02)\times10^{3}$.

Determination of the Specific Interfacial Area by the Turbidimetric Method

According to Eq. (1) and (5), d_{sv} *versus* log (I^{1590}/C^{2046}) should give a straight line.

$$\frac{6}{\rho_d d_{sv}} = 4505 + \log (I^{1590}/C^{2046}) \qquad (7)$$

Here, ρ_d was unity in this experimental condition. If one now uses this equation with measuring of the turbidity, I, and concentration, C, respectively, one obtains the value of mean surface-volume diameter of emulsion.

On the other hand, when the both values of d_{sv} and I are measured beforehand, the concentration of emulsion, C, can be calculated as following,

$$\log C = 0.777 \log I - 0.00293 \left(\frac{1}{\rho_d d_{sv}}\right) + 2.202 \qquad (8)$$

It has been demonstrated in this paper that quick measurements of the various average particle sizes of large (15—65 μm in diameter) spherical particles with broad size distributions are examined and then the calibration equations such as Eq. (5)—(7) can be established using the simple turbidimeter. However, it is necessary to measure the concentration of dispersed phase or the specific interfacial area of emulsion for the determination of such calibration curves. At any rate, because of their empirical nature, such calibration equations are valid for the investigation of the stability of emulsion or average diameter of droplets with using of the turbidimeter.

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