DROP SIZE DISTRIBUTION IN A LIQUID-LIQUID PHASE MIXING VESSEL

MASABUMI NISHIKAWA, FUYUHIKO MORI, TAKASHI KAYAMA AND SHIGERU NISHIOKA
Department of Nuclear Engineering, Kyushu University, Fukuoka 812

Key Words: Mixing, Liquid-Liquid Dispersion, Drop Size Distribution, Normal Distribution

The drop size distribution in a vessel is decided by the mutual relation between energy dissipation rate, residence time of drops at a certain location, break-up rate of drops and coalescence rate of drops. Experimental results so far, however, leave us far from an understanding of the precise mutual relation. Accordingly, the authors have made correlative equations representing the drop-size distribution under various mixing conditions. It is observed in this study that a combination of three normal distribution curves gives a good fit for the volumetric drop-size distribution and that the number distribution of drops is also given by a combination of two normal distribution curves.

Introduction

Knowledge of the size distribution or interfacial area of drops is required for prediction of heat and mass transfer phenomena in the liquid-liquid dispersion system in a mixing vessel. For instance, the performance of a mixer-settler in nuclear fuel reprocessing should be analyzed from drop size distribution for optimizing the extraction of uranium and plutonium. Effective extraction of tritium bred in the liquid lithium blanket of a fusion reactor should also be considered to decrease the tritium inventory in the solvent extraction process.

The drop-size distribution in a mixing vessel should be largely dependent on the micro- and macro-size turbulent motions and flow patterns in the mixing vessel because the mutual relation between energy dissipation rate, residence time of drops at a certain location in the mixing vessel, break-up rate of drops and coalescence rate of drops decides the distribution. However, the turbulent properties in the mixing vessel are so complicated, as reported by the present authors,[6,9] that no means of estimating the drop-size distribution curve in the mixing vessel has yet been developed. An empirical equation representative of the drop size distribution can therefore give useful information for optimization of actual processes or further research.

Drop-size distributions in the beeswax-hot water system are used in this work. Average drop size under break-up or coalescence conditions of this dispersion system are discussed elsewhere by the present authors.[7,8]

Chen and Middleman,[3] Brown and Pitt[1] and Carabrese *et al.*[2] reported that the volumetric drop size distribution in a liquid-liquid phase mixing vessel is represented by a normal distribution curve, though van Heuven and Hoevenaarj applied a gamma distribution curve.[10] In their correlations, however, only intermediate-size drops were taken into account; small- or large-size drops in distribution were excluded. It is observed in this work that a combination of three normal distribution curves can describe the whle volumetric drop size distribution from d_{pmin} to d_{pmax}.

The number distribution curves of drops in a mixing vessel are also correlated by a combination of two normal distribution curves in this work.

1. Background of This Work

As stated in the previous paper,[7] the largest drop size in a turbulent field under non-coalescence condition d_p^* is determined by the ratio of the kinetic energy of an oscillating drop due to turbulent fluctuation E_v and the energy due to interfacial tension E_s as

$$d_p^* \sim E_v/E_s \sim \varepsilon^{-2/5} \tag{1}$$

where ε is the local rate of energy dissipation per unit mass of the turbulent liquid.

Chen and Middleman[3] assumed that the probability density function of drops $P(d_p)$ was shown by some function of E_v/E_s in the break-up dominating region as

$$P(d_p) = \Phi(E_v/E_s) \tag{2}$$

Received July 10, 1990. Correspondence concerning this article should be addressed to M. Nishikawa. F. Mori is now at Fuji Film Co. Ltd., T. Kayama and S. Nishioka are now at Satake Chemical Equipment Mfg., Ltd.

where Φ is an unknown functional dependence.

Chen and Middleman, Brown and Pitt,[1] and Carabrese *et al.*[2] have reported that the drop sizes in a break-up dominant mixing vessel are normally distributed in volume and can be correlated by normalization with the Sauter mean drop size d_{p32} which is related to the average energy dissipation rate per unit mass of mixing liquid $\bar{\varepsilon}$ as

$$d_{p32} \sim \bar{\varepsilon}^{-2/5} \tag{3}$$

As has been pointed out by Nagata,[5] however, the normal distribution curve fitted for middle-size drops cannot describe the trends at the lower and higher ends of the measured distribution. Use of an average dissipation rate may not be rational to explain the whole drop size distribution because the local rate of energy dissipation in a mixing vessel varies by several orders of magnitude as reported by the present authors elsewhere.[9] Therefore, it is attempted in this work to obtain other normal distribution functions to describe the lower and higher ends of the volumetric drop-size distribution in a mixing vessel considering that the lower and higher ends correspond to locations with high dissipation rate and those with low dissipation rate, respectively.

In the meantime, the smallest drop size d_p^+ for which coalescence is slowed by turbulence is determined by

$$d_d^+ \sim E_v/E_{ad}$$
$$\sim \varepsilon^{-1/4} \tag{4}$$

where E_{ad} is the energy of adhesion between a pair of drops. The probability density function of drops in the coalescence dominating region may also be related to E_v/E_{ad} as in the case of drops in the break-up region.

2. Experimental

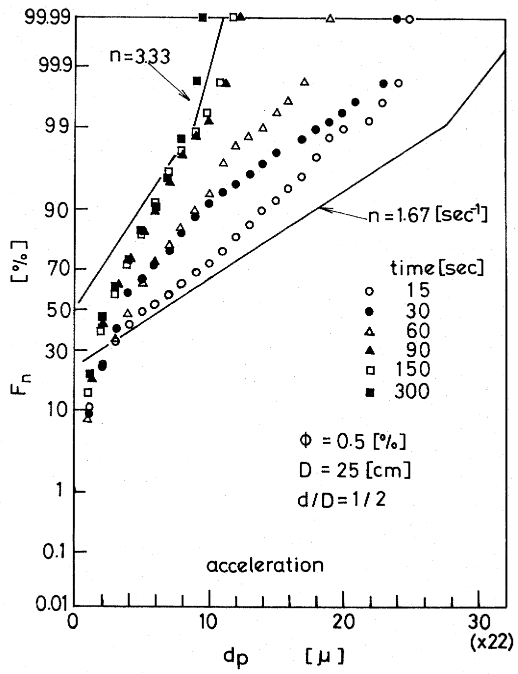
The mixing systems consisted of a cylindrical flat-bottomed stainless tank with a six-bladed stainless or brass Rushton-type turbine impeller used under the fully baffled condition. The vessel diameter was 12, 16, 25 or 50 cm and the liquid height was equal to the vessel diameter.

The continuous phase was hot distilled water and the dispersed phase was honeybee wax, the volumetric fraction of which was varied from 0.005 to 0.3. The size distribution of drops was evaluated by counting 500 to 2000 solidified wax particles using microscopic pictures on a Burkel-Turke blood-counting plate.

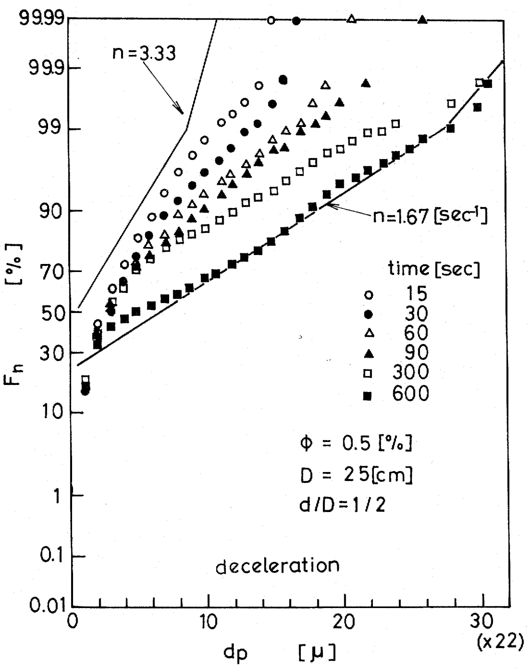
Details of the experimental methods was given in the previous reported about average drop sizes[7] and that about the scale-up effect of the mixing vessel.[8]

3. Results and Discussion

Firure 1 shows the change in pattern of drop-size distribution with time after sudden acceleration or deceleration of impeller speed. Application of Yamamoto's correlation for discharge flow rate[4] gives 8 seconds as the circulation time of mixing liquid for an impeller speed of 3 rps and 14 seconds for 1.67 rps. The time to reach a new steady-state distribution show that coalescence or break-up phenomena of drops proceed rather slowly compared to the circulation time



(a)



(b)

Fig. 1. Change of drop-size distribution with time after sudden change of impeller speed
a) acceleration of impeller speed
b) deceleration of impeller speed

of mixing liquid in these experiments. The average residence time of dispersions at a certain local point in the mixing vessel should be much smaller than the average circulation time. Accordingly, local drop size cannot be directly estimated from the turbulent energy dissipation spectra at that point because the residence time of mixing liquid is too short to experience full coalescence or break-up. It is also seen from Fig. 1 that the coalescence rate of large drops seem to be faster than that of small drops though no clear difference with drop size is observed for the break-up rate, and that the break-up of drops proceeds rather more rapidly than does the coalescence.

The above discussion implies that only a full understanding of the turbulent properties and the flow patterns throughout the mixing vessel can provide an estimation of the local drop-size distribution with knowledge of coalescence and break-up rate of drops under various conditions.

3.1 Volumetric drop-size distribution

Figure 2 shows the cummulative volumetric drop-size distribution plotted on a normal distribution graph for liquid-liquid dispersions of various volumetric fractions in the coalescence-dominant mixing conditions in a 25 cm vessel. In this plot the cummulative value up to the maximum drop size is plotted at the 99.99% point though the correct point is 100%. This figure implies that the drop sizes in a coalescence-dominant mixing vessel are also normally distributed in volume and that a combination of three norMal distribution curves can represent the whole volumetric drop-size distribution. The volumetric distribution curve shown in **Fig. 3** for various vessel sizes and various volumetric fractions also under coalescence-dominent mixing conditions give the results to support the consideration stated above.

The drop-size distribution is correlated using the normal distribution function.

$$f_v=(1/\sqrt{2\pi}\sigma_d)\exp(-(x-x_m)^2/2\sigma_d^2)\,, \tag{5}$$

$$F_v=\int f_v dx \tag{6}$$

where the average value x_m and the standard deviation σ_d are given by

$$x_m=d_{pmin}+\alpha(d_{pmax}-d_{pmin}) \tag{7}$$

and

$$\sigma_d=\beta(d_{pmax}-d_{pmin}) \tag{8}$$

d_{pmax} in above equations means the maximum drop size observed in the dispersion and is related to the Sauter mean drop size d_{p32} as

$$d_{p32}/d_{pmax}=0.45 \quad \text{(coalescence region)} \tag{9}$$

for the coalescence mixing region by the present

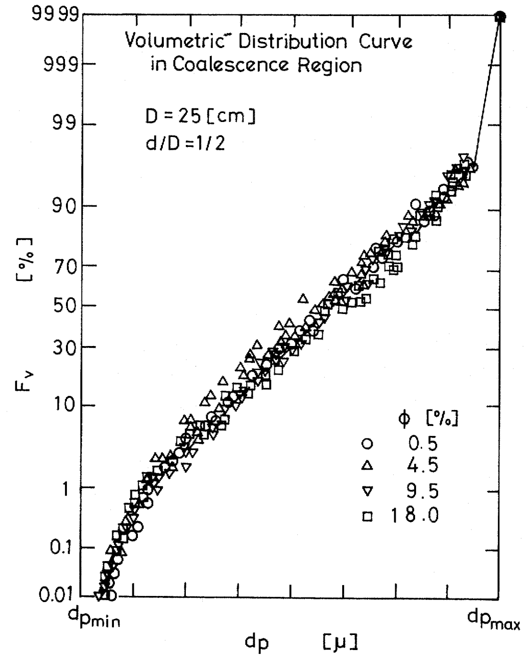


Fig. 2. Volumetric distribution curve for emulsion in coalescence-dominant region of a 25 cm vessel on normal-distribution graph

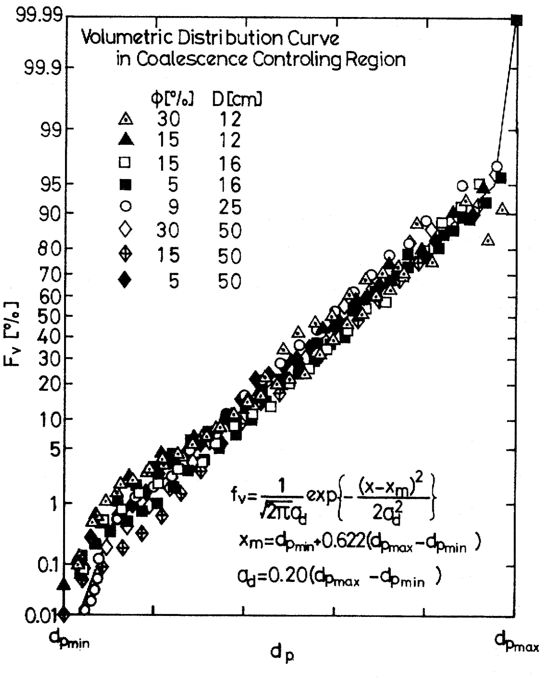


Fig. 3. Volumetric distribution curve for emulsion in coalescence-dominant region

authors.[7)]

The minimum drop size d_{pmax} observed in the beeswax-hot water system has an almost constant value of 8 microns, as was also reported in the previous paper. Accordingly, normalization of the volumetric drop-size distribution with d_{p32} in a coalescence-dominant mixing vessel is possible as in a break-up dominant mixing vessel.

Table 1. α and β for volumetric drop size distribution

	α $(=(x_m-d_{pmin})/(d_{pmax}-d_{pmin}))$	β $(=\sigma_d/(d_{pmax}-d_{pmin})$	volumetric fraction
Coalescence region			
small-size drops	0.28	0.066	<1%
intermediate-size drops	0.622	0.20	94%
large-size drops	0.90	0.025	5%
		$(d_{p32}/d_{pmax}=0.45)$	
Break-up			
small-size drops	0.17	0.047	1%
intermediate-size drops	0.56	0.21	94%
large-size drops	0.90	0.030	5%
		$(d_{p32}/d_{pmax}=0.5)$	

The values of 0.622 for α and 0.2 for β are obtained for the intermediate-size drops which occupy 94% of the volumetric fraction of dispersed phase in the coalescence-dominant mixing vessel.

The observed values for α and β for small drops, which occupy only 1% in volumetric fraction though account for half in number as stated later in this report, and values for large drops which occupy 5% in volumetric fraction though accounts for less than 1% in number are also listed in **Table 1**.

The combination of three normal distribution curves representing the whole drop-size distribution from minimum to maximum size drop can be estimated for various conditions using x_m and σ_d in this study because d_{pmin}, d_{pmax} and d_{d32} have already been correlated for various mixing conditions.[8)]

The volumetric drop-size distribution in the break-up dominant conditions shown in **Fig. 4** has almost the same tendency as observed in the coalescence-dominant conditions, and the values observed for α and β are also compared in Table 1.

The size of d_{pmax} in the break-up dominant mixing regions was related[8)] with d_{p32} as

$$d_{p32}/d_{pmax}=0.5 \quad \text{(break-up region)} \tag{10}$$

Comparison of drop-size distributions shown in **Fig. 5** shows that the volumetric fraction of small drops is a little larger in the break-up region than in the coalescence region and that the volumetric fraction of large drops is almost the same in both regions. The regions containing data observed in this work are indicated by hatched lines in this figure.

Correlated lines by Carabrese *et al.*[2)] and van Heuven and Hoevenaarj[10)] for the break-up region are compared in Fig. 5. The value for σ_d by Carabrese *et al.*, $0.24d_{p32}$, is almost half the value obtained in this work ($0.4d_{p32}$ for the break-up region and $0.46d_{p32}$ for the coalescence condition) for the volumetric size distribution of intermediate-size drops. Chen and Middleman[3)] and Brown and Pitt[1)] also applied a normal distribution curve for intermediate-size drops

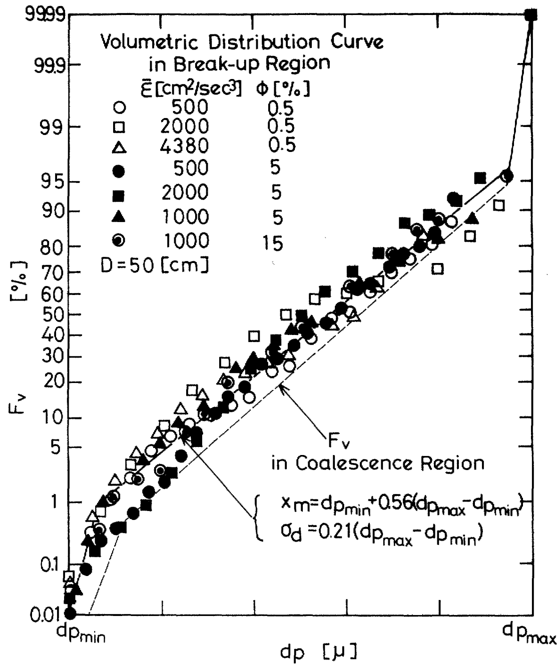


Fig. 4. Volumetric distribution curve for emulsion in break-up dominant region

in the break-up dominant mixing vessel and reported slightly smaller values for σ_d than those reported by Carabrese *et al.* though their values for d_{p32}/d_{pmax} were as large as around 0.67.

Disregarding drops smaller than about $0.2d_{p32}$ and drops larger than $1.8d_{p32}$ from the emulsion of drops observed in this work for the break-up region gives $0.115(d_{pmax}-d_{pmin})$ or $0.23d_{p32}$ for σ_d and the almost same normal distribution curve as that proposed by Carabrese *et al.*, Chen and Middleman, and Brown and Pitt is obtained. This means that disregarding small-size drops and large-size drops gives apparently a shaper normal distribution curve than the actual one.

The gamma distribution curve proposed by van Heuven and Hoevenaarj is said to be able to represent the drop size distribution from small-size to

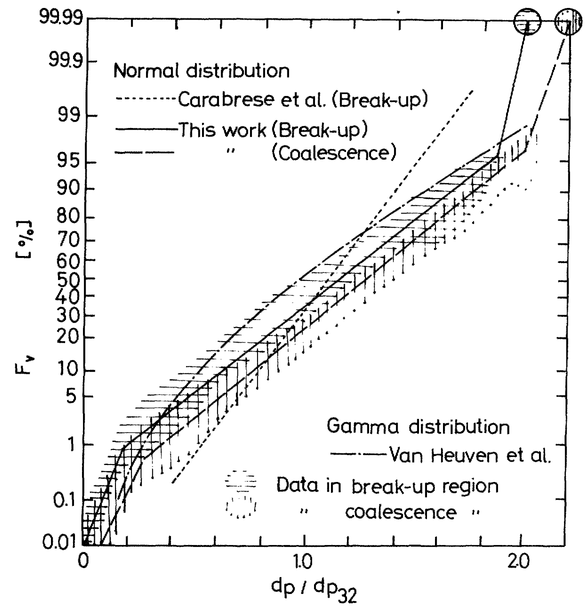


Fig. 5. Comparison of volumetric distribution curves by several authors in break-up region

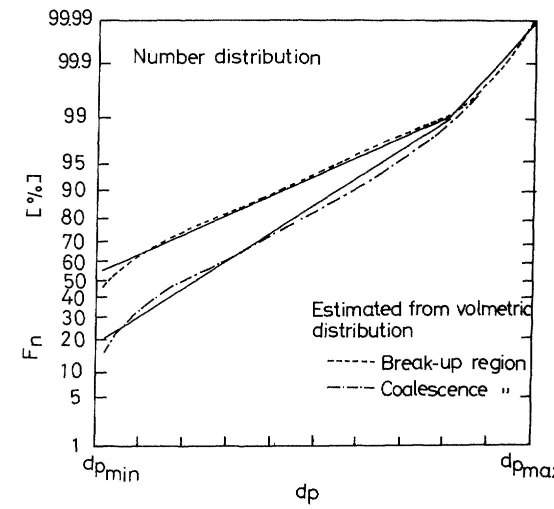


Fig. 6. Number distribution curves from volumetric distribution curves

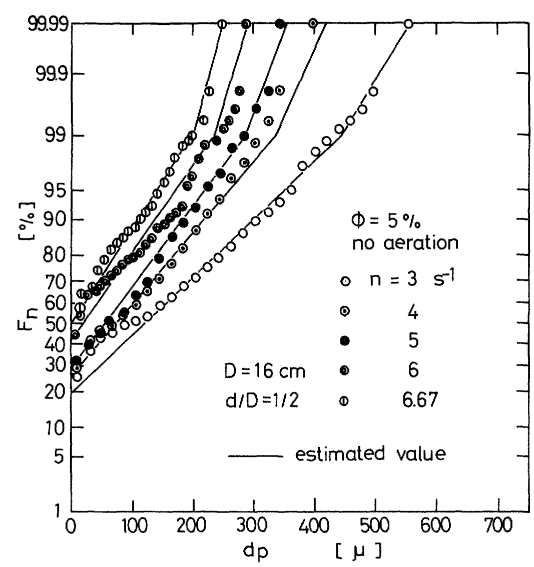


Fig. 7. Number distribution curve for emulsion on normal-distribution graph (effect of impeller speed)

intermediate-size drops as compared in Fig. 5. However, it is not recommended to apply the gamma distribution curve for the whole volumetric distributions because it cannot represent the large drops, which represent 5% in volume. The present authors could not obtain a gamma distribution curve suitable only for minimum to intermediate-size drops. Nagata also reported that the gamma distribution curve was good for smaller-size drops[5] than average value.

Accordingly, it is recommended in this report to apply a combination of three normal distribution curves to express the whole volumetric distribution of drops.

Normalization of the volumetric drop-size distribution is performed using $(d_p - d_{pmin})/(d_{pmax} - d_{pmin})$ in this work. Because a constant value of 8 microns has been observed for d_{pmin} in the dispersion system of this work, the comparison shown in Fig. 5 cannot be extended to the drop-size range where d_{pmin} is not negligibly small.

3.2 Number distribution of drops

From the volumetric distribution curve obtained in the coalescence or break-up region, the number-distribution curve for each region can be estimated as shown in **Fig. 6**. It is also known from this figure that each number distribution curve can be approximated by a combination of two normal distribution curves as shown by solid lines. However, it is observed in this work that use of normal distribution lines of which parameters are varied by energy dissipation rate or volume fraction of dispersed phase for smaller-size drops can give a better correlation than use of the number distribution curve estimated from the volumetric distribution curve.

Figures 7 and **8** show that the number distribution of drops in a mixing vessel can be approximated by a combination of two normal distribution curves. The cumulative value to the maximum drop size is plotted at the 99.99% point in these figures. Observations in this work show that x_m and σ_d in number distribution of drops are affected by the volumetric fraction of dispersed phase ϕ or average energy dissipation rate per unit mass of the mixing liquid $\bar{\varepsilon}$ though these parameters have no distinct influence on correlation of the volumetric distribution function when normalization with d_{pmax} or d_{p32} is applied.

x_m and σ_d for the number distribution of drops are correlated as follows in this work.

For $d_{pmin} < d_p < 0.8 d_{pmax}$

$$\alpha = 0.53(1 - 2.51 \times 10^{-5}\bar{\varepsilon})(1 + 0.40 \log \phi) \qquad (11)$$

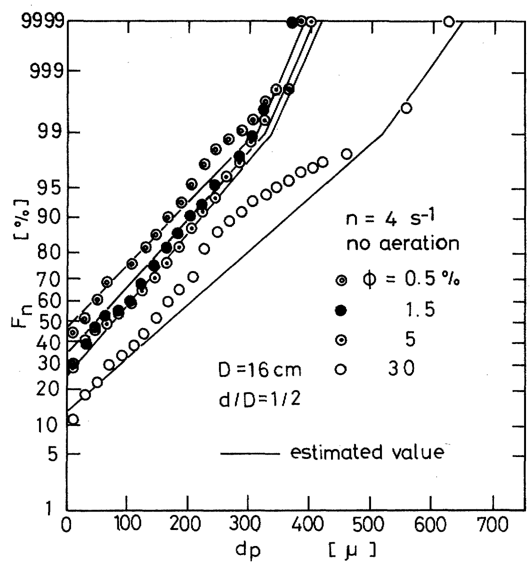


Fig. 8. Number distribution curve for emulsion on normal-distribution graph (effect of volumetric fraction)

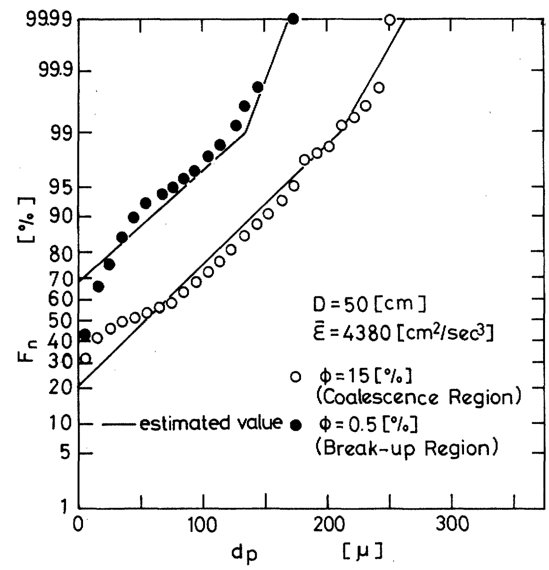


Fig. 9. Number distribution curve for emulsion in a 50 cm vessel on normal distribution graph

$$\beta = 0.074\bar{\varepsilon}^{0.1}(1 - 0.32 \log \phi) \quad (12)$$

For $d_p > 0.8 d_{pmax}$

$$\alpha = 0.47 \quad (13)$$

$$\beta = 0.14 \quad (14)$$

As the correlative equations for d_{pmin}, d_{pmax} and d_{p32} have been obtained already, the number-distribution curve can be predicted for various mixing conditions using the above equations. Experimental data shown in **Figs.** 7–**9** are satisfactorily represented by solid lines which are estimated by Eqs. (7)–(9), using the values for various drop sizes of which correlations are reported elsewhere.[7,8]

The above observation about the number-distribution curve implies that the small-size drops in a mixing vessel are not always formed in the same manner as the large-size drops, though the manner of energy balance to form larger drops decides the controlling phenomena in the volumetric distribution. The deviation in number distribution from the number distribution curve estimated from the volumetric distribution curve for small-size drops shows little deviation in the volumetric distribution curve.

As the smallest drop size in the emulsion is observed to be 8 microns in this work, the number-distribution curve of drops can be conveniently obtained on a normal distribution graph when the probability of d_{pmin} in number distribution, $f_{n,min}$, is evaluated because the normal distribution curve applied for drop sizes larger than $0.8d_{pmax}$ is not affected by ϕ and $\bar{\varepsilon}$ as shown by Eqs. (13) and (14).

This work gives the following equation.

$$f_{n,min} = 5.0\bar{\varepsilon}^{1/3} \exp(-0.55\phi^{1/3}) \quad \text{in } \% \quad (15)$$

The small drops occupy a large portion in the number distribution though they occupy only a small portion in the volumetric distribution. However, they are likely to produce undesirable effects in the extraction operation because of their slow coalescence rate.

4. Conclusions

The volumetric drop-size distribution in a liquid-liquid phase mixing vessel is represented by a combination of three normal distribution curves regardless of the controlling phenomena in drop formation. The first curve is for small-size drops, which occupy almost half in number though less than 1% in volumetric fraction. The second one is for intermediate-size drops, which account for 94% in volumetric fraction. The third one is for large drops, which occupy about 5% in volumetric fraction though only 1% in number. Disregarding the large- and small-size drops gives too sharp a normal distribution for the intermediate-size drops.

The number distribution curve can be represented by a combination of two normal distribution curves.

Nomenclature

D	=	vessel diameter	[cm]
D_0	=	reference vessel diameter	[cm]
d	=	impeller diameter	[cm]
d_p	=	drop size	[cm]
d_{pmax}	=	maximum drop size in emulsion	[cm]
d_{pmin}	=	minimum drop size in emulsion	[cm]
d_{p32}	=	Sauter mean drop size of emulsion	[cm]
E_{ad}	=	energy of adhesion	[g·cm²/²]
E_s	=	energy due to interfacial tension	[g·cm²/s²]
E_v	=	kinetic energy of oscillating drop	[g·cm²/s³]
F	=	cumulative probability function	[—]
f	=	probability distribution function	[—]

n	=	impeller speed	[s^{-1}]
x_m	=	average drop size	[cm]
α	=	function defined in Eq. (7)	[—]
β	=	function defined in Eq. (8)	[—]
σ	=	interfacial tension	[g/s^2]
σ_d	=	standard deviation	[—]
ε	=	local rate of energy dissipation	[cm^2/s^3]
$\bar{\varepsilon}$	=	average energy dissipation rate per unit mass of mixing liquid	[cm^2/s^3]
Φ	=	unknown function	
ϕ	=	volumetric fraction of dispersed phase	[%]
ρ	=	specific weight	[g/cm^3]

⟨suffix⟩

n	=	number distribution of drops
v	=	volumetric drop-size distribution

Literature Cited

1) Brown, D. E. and K. Pitt: *Chem. Eng. Sci.*, **82**, 345 (1974).
2) Carabrese, R. V., T. P. K. Change and P. T. Dang: *AIChE J.*, **32**, 657 (1986).
3) Chen, H. T. and S. Middleman: *AIChE J.*, **13**, 989 (1967).
4) Nagata, S., K. Yamamoto, K. Hashimoto and Y. Naruse: *Kagaku Kogaku*, **23**, 595 (1959).
5) Nagata, S.: Mixing, Halsted Press (Kodansha), Tokyo, 1975
6) Nishikawa, M., Y. Okamoto, K. Hashimoto and S. Nagata: *J. Chem. Eng. Japan*, **9**, 489 (1976).
7) Nishikawa, M., F. Mori and S. Fujieda: *J. Chem. Eng. Japan*, **20**, 82 (1987).
8) Nishikawa, M., F. Mori, S. Fujieda and T. Kayama: *J. Chem. Eng. Japan*, **20**, 454 (1987).
9) Okamoto, Y., M. Nishikawa and K. Hashimoto: *Int. Chem. Eng.* **21**, 88 (1981).
10) van Heuven, J. W. and J. C. Hoevenaarj: *Proc. 4th Int. Symp. Reactor Eng.*, Bruxelles (1969).