On the other hand, *a priori* criteria have been reported recently (Huang and Varma 1981a) applying the fast pseudo-first-order reaction model (model 1f) in a nonadiabatic gas-liquid CSTR to provide necessary and sufficient conditions among physico-chemical parameters which assure unique and multiple steady states, and also the asymptotic stability of the steady states. It is believed that these *a priori* criteria can be derived only by assuming the pseudo-first-order reaction in the "fast" reaction regime (i.e., the fast pseudo-first-order reaction model). Therefore, the use of the fast pseudo-first-order reaction model is justifiable not only because of the fair agreement between the multiplicity regions predicted by this model and the second-order reaction model, but also because of its capability to lead to *a priori* criteria, as shown by the analyticity of the uniqueness and multiplicity regions presented in this work.

Thus, it is recommended that the fast pseudo-first-order reaction model (model 1f) be always applied first to give an idea of the multiplicity regions of second-order reactions; if specific operational conditions are close to regions of multiplicity predicted by this model, then a fine tuning can be done to identify the possibility precisely by using the pseudo-first-order reaction model (model 1) and the full second-order reaction model (model 2)—in that order. Although both models 1 and 2 use trial-and-error, the computational effort is significantly lower for model 1.

ACKNOWLEDGMENT

The Union Oil Fellowship in Reaction Engineering and a Reilly tuition scholarship for D. T.-J. Huang is gratefully acknowledged.

NOTATION

Only those symbols not reported in Part I of this work (Huang and Varma, 1981b) are listed below.

F_{l1}, F_{l2} = critical liquid flow rates, defined by Eq. 4
Da_1, Da_2 = critical values of Da, defined by Eq. 5

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Liquid-Liquid Dispersion in Turbulent Couette Flow

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A dimensionless dispersion number was developed to characterize liquid-liquid dispersions created in turbulent Couette flow with respect to their subsequent coalescence in a settling zone. For a given solvent pair and continuous phase, the dispersion number is relatively constant over a wide range of operating and dimensional parameters. Because of this, the dispersion number can be used for the design and scale-up of liquid extraction equipment with discrete stages.

SCOPE

Couette flow is the name applied to flow in the annular region between two cylinders when one cylinder is rotating. When the rotational speed is sufficient, the flow becomes turbulent and can be used to disperse one liquid in another. This turbulent Couette mixing is an integral part of a centrifugal contactor for solvent extraction developed by Bernstein et al. (1973). In this work, our objective was to develop an understanding of the Couette mixing zone so that (1) the design of the Couette mixing zone can be put on a firm basis and (2) the liquid-liquid dispersion so formed could be related to its subsequent rate of coalescence in the separating zone.

Only the work of Clay (1940) reports on the use of a turbulent Couette mixer to produce a liquid-liquid dispersion. In that study, there was no flow through the mixer. Previous characterizations of liquid-liquid dispersions were made on the basis of: (1) the drop size or interfacial area or (2) the time for the emulsion to break. The use of drop size or interfacial area was avoided in the present work because of the time required to make such measurements and the limited usefulness of such results when mass transfer rates are high. On the other hand, the time for the emulsion to break is easy to measure and has been reported by many persons including Rodger et al. (1956), Ryon et al. (1959), Groenier (1968), and Barnea and Mizrahi (1975). The limitation of this measurement is that the time for an emulsion to break is very specific to the liquids used, the type of mixer, and the type of settling zone. In addition, it has not been clear how the results of this batch test apply to a continuous-flow system.

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In all the tests reported here, the inner cylinder (rotor) is the rotating cylinder. Rotor diameters were varied from 2 to 25 cm and the diameter ratio of the inner cylinder divided by the outer cylinder was varied from 0.49 to 0.88. (The actual gap between the cylinders varied from 3.3 to 23.6 mm.) The ratio of mixing zone height to rotor diameter was varied from 1.05 to 1.91 as needed to accommodate the dispersion level in the Couette mixing zone. Rotor speeds from 62.8 to 628 rad/s (600 to 6000 rpm) were used in the tests while flow rates ranged from 3.3 to 2000 cm^3/s (0.2 to 120 L/min). The aqueous phase contained nitric acid at concentrations of either 0.5 $\underline{M}$ or 3.0 $\underline{M}$. The organic phase was 30 vol. % tri-*n*-butyl phosphate (TBP) in *n*-dodecane (*n*DD). Dispersion coalescence was tested in batch and flow systems. Both gravity (9.81 m/s^2) and centrifugal (up to 2310 m/s^2) fields were used in the coalescence tests.

Turbulent Couette mixing represents a type of mixing which has been largely neglected in the literature. While the present work is focused on liquid-liquid dispersion which is of particular interest in discrete-stage solvent extraction, direct-contact heat transfer, and emulsion polymerization, the results should be applicable to a much wider range of liquid mixing problems.

CONCLUSIONS AND SIGNIFICANCE

A new dimensionless number was developed for characterizing dispersions. This dispersion number is given by:

$$N_{Di} = \frac{1}{t_R}\sqrt{\frac{\Delta Z}{a}}$$

where a is the acceleration on the coalescing dispersion, t_R is the average residence time in the coalescing dispersion band within the separating zone of a flowing system or the time to break in a batch system, and ΔZ is the thickness of the dispersion band in the separating zone of a flowing system or the initial thickness of the dispersion in a batch system. For a given continuous phase, we found that N_{Di} is essentially constant over the entire range of turbulent Couette mixing conditions studied. Further a review of the literature indicates that N_{Di} does not vary much with mixer type. A potential method for even more detailed dispersion characterization is explored.

From the results, the turbulent Couette mixer is shown to produce good liquid-liquid dispersions in small holdup volumes at high throughput with low pressure drop. The mixer is relatively insensitive to the feed port location, to the dimensions of the rotor, and to the gap between the rotor and the stationary outer cylinder. Thus, the turbulent Couette mixer with its intense mixing, low residence time, and unique shape represents an important new mixer design for the chemical process industry.

Because the dimensionless dispersion number is content over a wide range of Couette mixing conditions, it can be used for the design and scale-up of the settling-zone volume needed to coalesce liquid-liquid dispersions. The dispersion number incorporates the time for an emulsion to break in such a way that both batch and flow operations give the same N_{Di} values for a particular liquid system. In addition, results from both gravitational and centrifugal setting fields give the same N_{Di} value. Finally, a review of the literature for the very different liquid pairs used in solvent extraction should that N_{Di} values do not vary much, having a typical range from 0.0005 to 0.004 regardless of the type of mixer used. The full range of N_{Di} values calculated from the literature goes from 0.0001 to 0.020. At the lowest N_{Di} values, there is indirect evidence of significant resistance to droplet coalescence. Thus, N_{Di} is an important new tool in the evaluation of mixing equipment and in the design of separating zones for liquid-liquid dispersions.

Our interest in liquid-liquid dispersion in turbulent Couette flow is a direct result of our work on centrifugal contactors for solvent extraction. Initially, the contactor developed at Savannah River Laboratory (SRL) had a paddle mixer below the centrifuge. The mixer was attached to the centrifuge as described by Webster et al. (1969). At Argonne National Laboratory (ANL), Bernstein et al. (1973) modified the design so that the paddle mixer was replaced by a Couette mixer, which is simply the annular gap between the rotating centrifuge (rotor) and the centrifuge housing. The ANL or annular centrifugal contactor, shown schematically in Figure 1, reduces the cost of contactor construction and simplifies maintenance.

The annular centrifugal contactor operates in the following manner. The two immiscible phases to be contacted are fed to the annular or Couette mixing zone through the aqueous (or more dense phase) and organic (or less dense phase) inlets. The phases are mixed here and flow by gravity into the separating zone of the rotor. To allow the spinning liquid in the Couette mixing zone to reach the rotor inlet, stationary radial vanes are attached to the housing under the rotor. As the dispersion (unstable emulsion) coalesces in the separating zone of the rotor, a weir system at the top of the rotor allows the separated heavy and light phases to be discharged to the aqueous and organic collector rings, respectively. In multistage countercurrent operation, the liquids then flow by gravity to adjoining contactors. Thus, each contactor is a Couette mixer, a centrifugal settler, and a pump, all powered by a common drive shaft.

While the annular centrifugal contactor is understood in qualitative terms and has been demonstrated in practice by Bernstein et al. (1973), there is a need to characterize the dispersion leaving the Couette mixing zone in such a way that the capacity of the separating zone can be calculated. If the method of characterizing the dispersion is general enough, it should also apply to flow systems with gravity settling zones, that is, to the

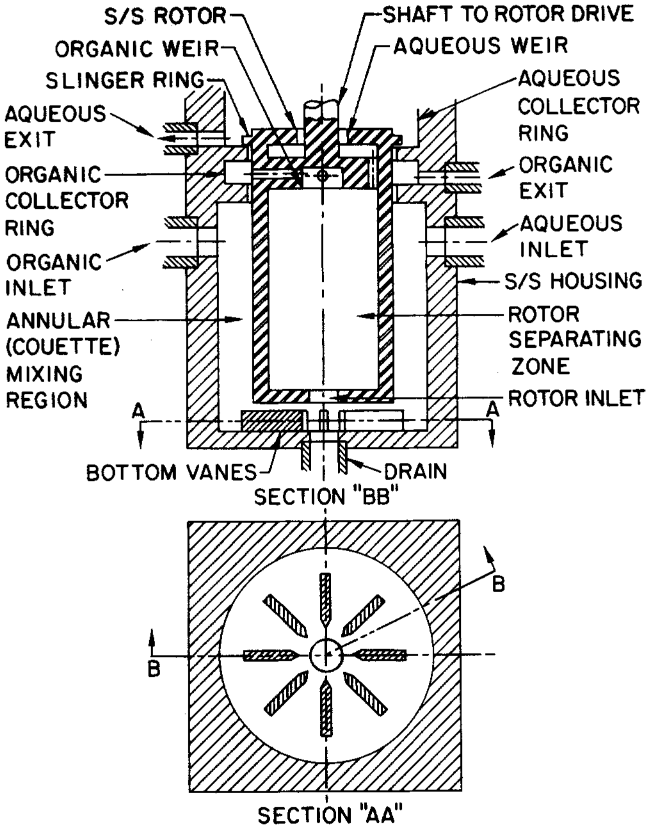

Figure 1. Schematic of annular centrifugal contactor.

design of mixer-settlers. Finally, for convenience in obtaining basic design data, the method should also be applicable to batch settling data. In this paper, we develop such a method for characterizing liquid-liquid dispersions and apply it to the dispersions formed in turbulent Couette flow.

RELATED WORK

The structure of the dispersion band (unstable emulsion band) in an operating gravity settler was studied in great detail by Barnea and Mizrahi (1975). They showed that the dispersion band is fairly uniform in composition and has an organic-to-aqueous ratio close to that of the feed ratio. However, adjacent to the separated dispersed phase, the dispersion band has a sublayer containing a much higher fraction of the dispersed phase. This sublayer forms a coalescing front with the separated dispersed phase. When the dispersed phase volume being fed to the settler is low, about 20% of the total volume, the sublayer does not form.

Mizrahi and Barnea (1970) developed a standardized batch test that measures the time for the dispersion to break. With this test, it is possible to calculate the flow capacity of the above-mentioned gravity settler. The correlation is limited because it does not include the depth of the settling zone. One depth was chosen for their batch tests. A second depth was chosen for their continuous-flow gravity settler tests. These arbitrarily chosen depths were then held constant for subsequent correlation of the data.

Another use for the batch settling time, as shown by Rodger et al. (1956), is in characterizing the interfacial area of a liquid-liquid dispersion. However, since this settling time did not fit into any of the existing dimensionless groups used in the interfacial-area correlation, they found it necessary to create a new dimensionless group by dividing the settling time by an arbitrarily chosen reference time.

DISPERSION NUMBER

Review of this related work indicated the need for a dimensionless number that would include the time required for a dispersion to settle. Such a number should, by its nature, reflect the fineness of the drop size of one phase dispersed in another, and hence, the degree of mixing obtained.

To form this dimensionless dispersion number, two times are identified. One is the residence time of the dispersion in the separating zone of a flowing system. In a batch operation, this is the time for the dispersion to break t_B. The other is the time for a droplet to travel the thickness of the separating (settling) zone. For a given liquid pair for which Stoke's law (Perry and Chilton, 1973) applies, this travel time should be inversely proportional to the acceleration a and the square of the drop diameter, and directly proportional to the thickness ΔZ of the dispersion in the settling zone. Our experience with centrifugal contactors suggests that capacity q is proportional to the square root of the acceleration rather than the first power of the acceleration. On this basis, a dimensionless dispersion number was proposed as:

$$N_{Di} = \frac{1}{t_B}\sqrt{\frac{\Delta Z}{a}} \tag{1}$$

or as:

$$N_{Di} = \frac{q}{V}\sqrt{\frac{\Delta Z}{a}} \tag{2}$$

for batch and continuous flow systems, respectively. On the same basis, for a given liquid pair, N_{Di} should be inversely proportional to drop size, but otherwise fairly constant.

By introducing the concept of residence time t_R, the dispersion number can be expressed in the more general form:

$$N_{Di} = \frac{1}{t_R}\sqrt{\frac{\Delta Z}{\bar{a}}} \tag{3}$$

where Eq. 3 becomes either Eq. 1 or 2 for batch and flow systems, respectively. For batch systems, t_B is the time for the dispersion to break and includes the total thickness of the dispersion in the container immediately after the dispersion is formed. For flow systems, V is the volume of the dispersion band in the separating zone. If the dispersion band is not well positioned, the separating zone will not be fully used and the settler capacity will be reduced accordingly. For centrifugal contactors, the use of air-controlled weirs as shown by Webster et al. (1969) allows the dispersion band to be positioned for maximum utilization of the separating zone. In this case, V becomes the volume of the separating zone when the contactor is being operated at its full capacity.

Acceleration in gravity settlers is simply g. In centrifugal settlers, the acceleration is given by $r\omega^2$ and so varies within the settler. A volume-average acceleration given by:

$$\bar{a} = \bar{r}\omega^2 \tag{4}$$

where

$$\bar{r} = \frac{\int_{r'_o}^{r_u} 2\pi\, r^2 dr}{\int_{r'_o}^{r_u} 2\pi\, r\, dr} = \frac{2}{3}\left(\frac{r_u^3 - r'^3_o}{r_u^2 - r'^2_o}\right) \tag{5}$$

should be used. As a first approximation, $\bar{r}$ can be calculated as the arithmetic average of r_u and r'_o. When r_u is twice r'_o, the error in calculating N_{Di} in this manner is less than 2%.

ANALYSIS

The dimensionless dispersion number given by Eq. 3 is a simplified version of the ratio of the settling time t_s to the residence time. The complete ratio should be unity if a separat-

TABLE 1. COUETTE MIXER DIMENSIONS

Mixer Code	$r_{R,o}$, mm	$r_{H,i}$, mm	Δr_c, mm (in.)	n	ΔH_c, mm	ΔH_g, mm	L_c, mm	V, cm^3	Alternate Mixer Code
Rotor II[a]	11.0	14.3	3.3 (1/8)	8	2.4[b]	0.8[b]	23.1	3.6	20 mm
		15.9	4.9 (3/16)	8	2.4[b]	0.8[b]	23.1	3.6	20 mm
		17.5	6.5 (1/4)	8	2.4[b]	0.8[b]	23.1	3.6	20 mm
		22.2	11.2 (7/16)	8	2.4[b]	0.8[b]	23.1	3.6	20 mm
Rotor III	11.0	15.9	4.9 (3/16)	8	2.4	0.8	29.9	5.4	20 mm
94 mm	47.6	54.0	6.4 (1/4)	4	10.2	1.3	181.4	980	9 cm
262 mm	132.5	156	23.6(0.929)	8	17.5	0.8	348	16140	25 cm

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[a] As indicated, four housings are available so that Δr_c can be varied from 3.3 to 11.2 mm.
[b] These dimensions were used except where specifically stated otherwise.

ing zone is operating at capacity, so that we can write

$$t_s = t_R \tag{6}$$

which becomes

$$\frac{\Delta Z}{U} = \frac{V}{q} \tag{7}$$

for flow systems, and

$$\frac{\Delta Z}{U} = t_B \tag{8}$$

for batch systems. While use of Eqs. 7 and 8 would be desirable, it is hard to evaluate U. By using N_{Di} instead of U for a given liquid pair, their physical properties can be ignored and drop diameter need not be measured. In fact, changes in N_{Di} should reflect changes in drop diameter and thus provide an indirect way of measuring drop diameter. Thus, a more detailed evaluation of the terminal droplet velocity U is appropriate to find the proper dependence of N_{Di} on the droplet diameter d. This analysis of U, in turn, forces a further evaluation of the thickness ΔZ of the dispersion band.

TERMINAL DROPLET VELOCITY

Terminal velocity correlations for single liquid drops immersed in an insoluble liquid are given by Klee and Treybal (1956). They follow the form of U for rigid particles given by Stoke's law:

$$U = \sqrt{\frac{4\,\bar{a}\;d\,\Delta\rho}{3\,\rho_c\,C}} \tag{9}$$

with a new C correlation for liquid droplets. When the drop size is below a critical diameter given by:

$$d_c = 0.33\,\rho_c^{-0.14}\Delta\rho^{-0.43}\,\mu_c^{0.30}\,\sigma^{0.24} \tag{10}$$

then C is given by:

$$C = \frac{1.819\,\mu_c^{0.19}\,\sigma^{0.03}}{d^{0.23}\,U^{0.26}\,\rho^{0.23}} \tag{11}$$

and U becomes:

$$U = \frac{0.837\,\bar{a}^{0.57}\,(\Delta\rho)^{0.57}\,d^{0.70}}{\rho_c^{0.44}\,\mu_c^{0.11}\,\sigma^{0.02}} \tag{12}$$

For the systems tested here, $\rho_c \cong 1000$ kg/m^3, $\Delta\rho \cong 170$ kg/m^3, $\mu_c \cong 0.001$ Pa·s and $\sigma \cong 0.01$ N/m, so that $d_c \cong 3.1$ mm. Using the method of Baird (1979), the value of the average drop diameter should be in the range of 0.02 to 0.05 mm in the mixing zone, which is well below the critical drop size.

Eq. 12 shows that, for droplets, U is roughly proportional to the square root of $\bar{a}$, rather than the first power of $\bar{a}$ as given by Stoke's law for rigid particles. Thus, since Eq. 12 has the acceleration term to about the same power as it appears in N_{Di}, the equation can be used to show that N_{Di} should vary inversely with $\rho_c^{0.44}$, $\mu_c^{0.11}$, and $\sigma^{0.02}$. Also N_{Di} should be directly proportional to $\Delta\rho^{0.57}$ and $d^{0.70}$. Thus, for a given liquid pair, decreasing values of d as mixing increases should be reflected in decreasing values of N_{Di}.

DISPERSION-BAND THICKNESS

To obtain the effect of dispersion-band thickness ΔZ on t_B, Eq. 12 is combined with Eq. 8. This shows t_B to be proportional to ΔZ rather than to $\Delta Z^{0.5}$ or to $\Delta Z^{0.7}$ given by the experimental data below. This problem of determining the proper exponent for ΔZ is resolved by following the analysis of Barnea and Mizrahi (1975). They take into account a close-packed droplet bed where the rate of coalescence and relative velocities of the continuous and dispersed phases are important. The result of their analysis is:

$$\Delta Z \propto \left(\frac{q}{A}\right)^y \tag{13}$$

where

$$y = \frac{j}{i} + 1 \tag{14}$$

In this equation, j is a measure of the rate of drop coalescence and has the range:

$$j \geq 3 \tag{15}$$

When essentially all droplet collisions result in coalescence, $j = 3$. When significant bouncing occurs, j increases. The i in Eq. 14 is a function of the drop Reynolds number $N_{Re,d}$ and has the range:

$$0.5 \leq i \leq 2 \tag{16}$$

TABLE 2. LIQUIDS TESTED

Aqueous Phase
A_1: 0.5 mol Nitric Acid/dm^3 Solution (94-mm and 262-mm Tests)
A_2: 3.0 mol Nitric Acid/dm^3 (20-mm Tests)
Organic Phase
O_1: 30 vol. % Tri-*n*-Butyl Phosphate (TBP) in *n*-Dodecane (*n*DD)

Phase	ρ, kg/m^3	μ, Pa · s
A_1	1016	0.001
A_2	1098	0.001
O_1	826	0.002

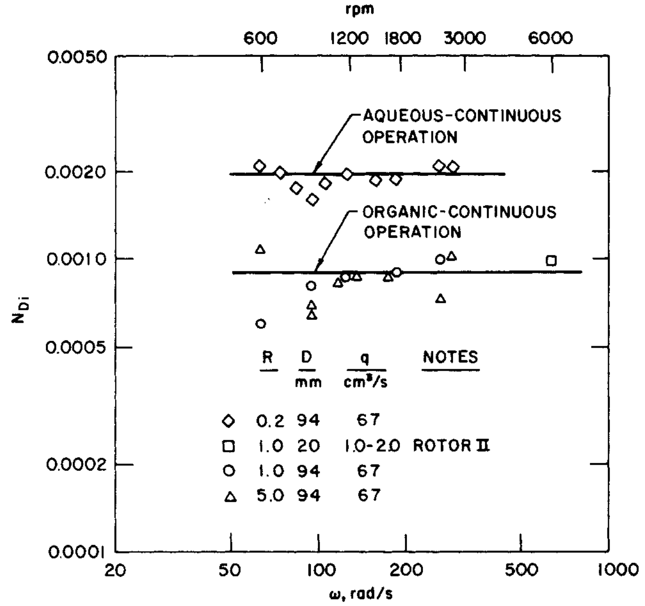

Figure 2. Effective of Couette mixer speed on the dispersion number, Δr_c = 6.4 mm. $\bar{a}$ = 9.81 m/s². Continuous phase is aqueous continuous for R = 0.2 and organic continuous for higher R values.

At $N_{Re,d}$ values less than 0.1, $i = 2$. When $N_{Re,d}$ increases to values of 5 and 50, i decreases to 1.5 and 1.0, respectively. Finally, at very turbulent flows, which are too high to be of interest here, $i = 0.5$. Barnea and Mizrahi's review of the literature shows that y values are typically in the range of 2 to 3, generally around 2.5. However, they report some y values that are twice this value. In no case do they report any lower y values. Their theory gives a minimum y value of 2.5 when both $N_{Re,d}$ is low, so that $i = 2$ and the drops coalesce easily, so that $j = 3$. As $N_{Re,d}$ increases or the rate of coalescence decreases, y will increase.

When $y = 2$, and when both N_{Di} and the accelerational field are constant, the proportion given by Eq. 13 is identical to that given by Eq. 2. In general, Eq. 13 predicts that

$$N_{Di} \propto \Delta Z^{c} \tag{17}$$

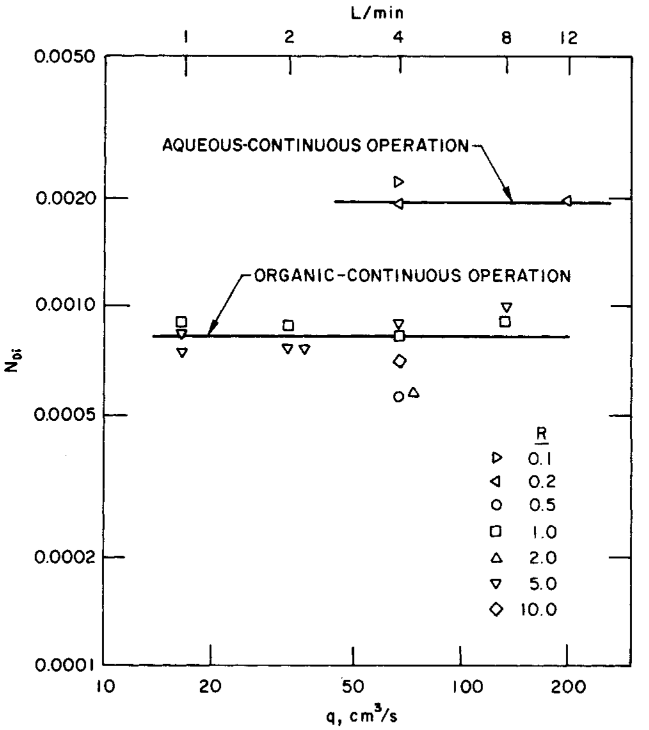

Figure 3. Effect of throughput and O/A ratio on the dispersion number. D = 94 mm. ω = 184.8 rad/s (1765 rpm). $\bar{a}$ = 9.81 m/s². Continuous phase is aqueous continuous for R of 0.1 and 0.2 and organic continuous for higher R values.

where

$$c = 0.5\,\frac{\left(\frac{j}{i} - 1\right)}{\left(\frac{j}{i} + 1\right)} \tag{18}$$

so that c has the range

$$0.1 \le c < 0.5 \tag{19}$$

Thus, if $j = 3$ and i drops from 2 to 1.5 to 1.0, c increases correspondingly from 0.10 to 0.17 to 0.25 (y increases correspondingly from 2.5 to 3 to 4). Thus, based on these results of Barnea and Mizrahi (1975), N_{Di}, which already includes $\sqrt{\Delta Z}$, is expected to have some slight additional dependence on ΔZ.

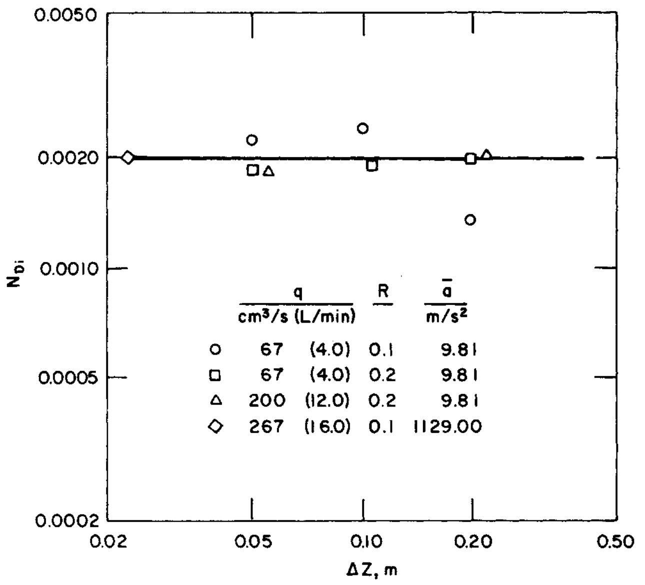

Figure 4. Variation of dispersion number with dispersion-band thickness in aqueous-continuous operation. D = 94 mm. ω = 184.8 rad/s (1765 rpm).

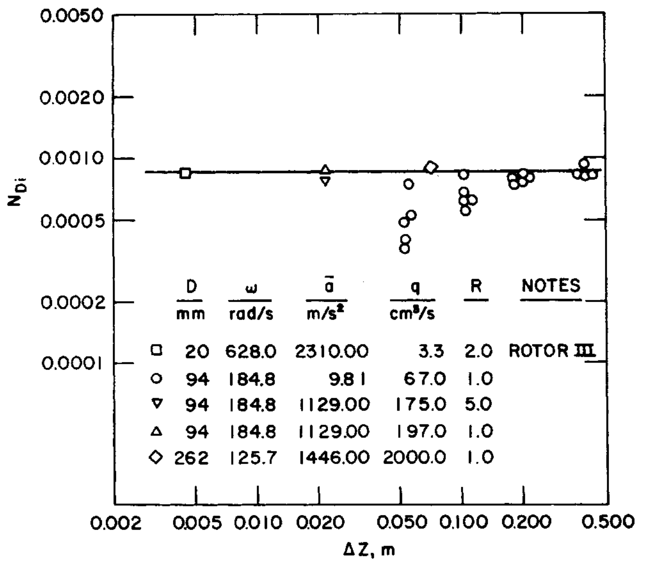

Figure 5. Variation of dispersion number with dispersion-band thickness in organic-continuous operation.

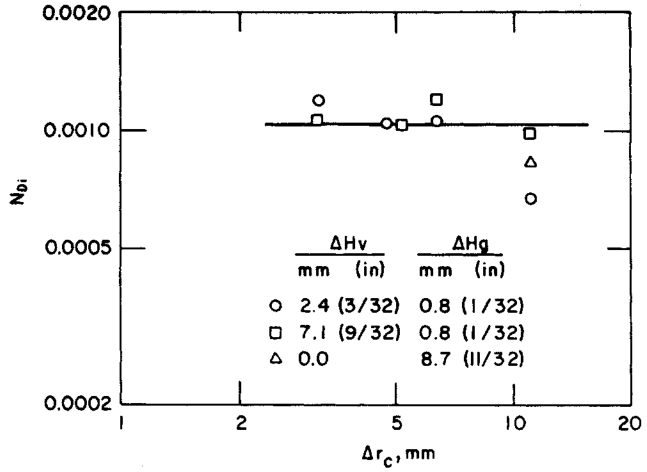

Figure 6. Effect of Couette mixer gap on the dispersion number. D = 20 mm (Rotor II). ω = 628 rad/s (6000 rpm). q = 1.0 – 2.0 cm^3/s (60 – 120 mL/min). Organic-continuous operation with R = 1.0. $\bar{a}$ = 9.81 m/s^2.

EXPERIMENTAL

To generate the liquid-liquid dispersions, Couette mixers of the type shown in Figure 1 were used in all tests. In this design, the rotor turns and the housing is fixed. Dimensions of the various Couette mixers are shown in Table 1. The liquids are listed in Table 2. Rotor speed could be varied from 314 to 942 rad/s (3000 to 9000 rpm) in the 20-mm mixers, from 62.8 to 314 rad/s (600 to 3000 rpm) in the 94-mm mixer and from 62.8 to 151.8 rad/s (600 to 1450 rpm) in the 262-mm mixer. Speed was checked with a General Radio stroboscopic tachometer (Model 1531 AB "Strobotac"). Tests in the 20-mm mixers were made at flow rates from 0.08 to 3.33 cm^3/s (5 to 200 mL/min), using FMI (Fluid Metering, Inc., Oyster Bay, NY) positive-displacement rotary piston pumps. In the 94-mm mixer, flow rates were varied from 7 to 267 cm^3/s (0.4 to 16 L/min), using constant head feed tanks with glass-tube variable-area flowmeters. Phase continuity is established by letting only the desired continuous phase flow into the mixing zone, so that the other phase is flushed out. Then the flow of the second phase is restarted and it disperses into the first phase. Phase inversion will occur only if the first phase as a continuous phase is inherently unstable at the operational O/A ratio.

Measurement of the dispersion number by gravity-settling batch tests was done as follows. The drain below the rotor, which is normally closed, was opened and some of the liquid-liquid dispersion from the Couette mixing zone was collected in a graduated cylinder or similar device. For the 94-mm and 262-mm tests, tubes 25 mm in diameter were used with liquid heights of 50, 100, 200, and 400 mm. The total time for the dispersion to break is measured with the start of settling adjusted for the time required to fill the cylinder. To develop a further, more elaborate, characterization of the dispersion, the dispersion band thickness is measured as a function of time at specific time intervals. The amount of

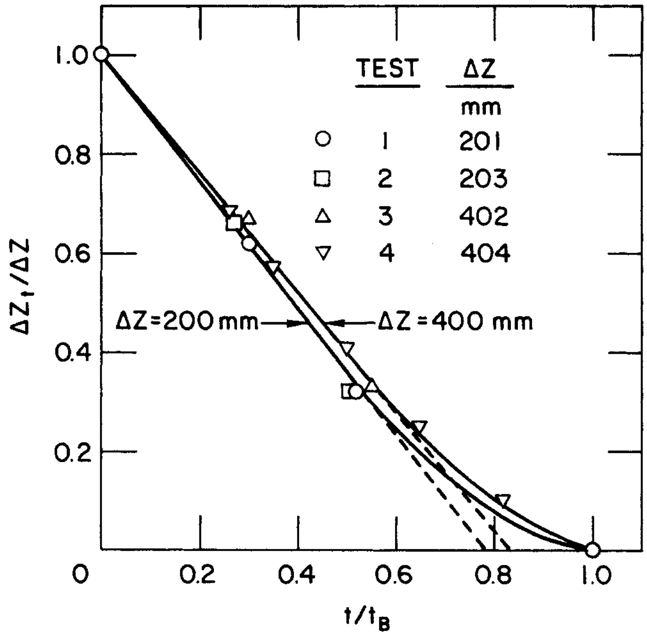

Fig. 7. Correlation of dispersion band coalescence with time.

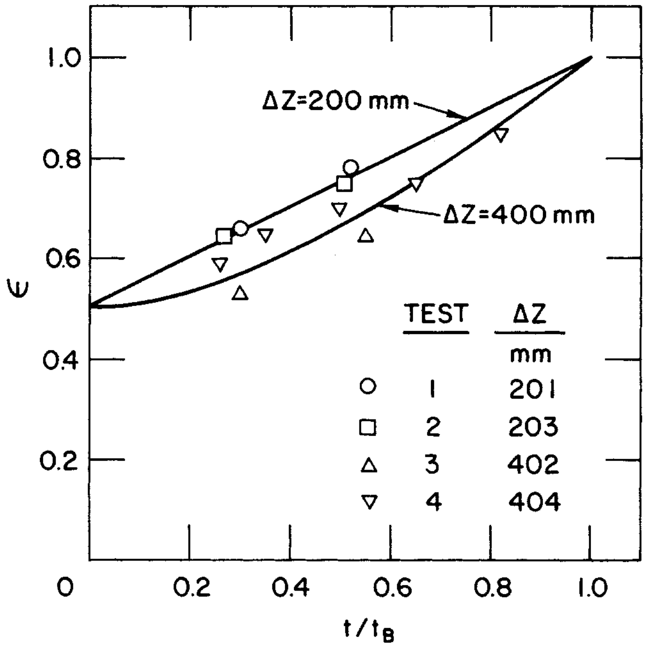

Fig. 8. Correlation of dispersed phase concentration with time in a coalescing dispersion band.

TABLE 3. ANALYSIS OF DISPERSION BAND COALESCENCE

D = 94 mm
R = 1.0 (Organic-Continuous Operation)
q = 67 cm^3/s (4.0 L/min)
ω = 184.8 rad/s (1765 rpm)
$\bar{a}$ = 9.81 m/s^2

Test	ΔZ, mm	T, °C	t_B, s	$t_{B,e}$, s	Δt, s	$N_{Di} \times 10^5$	$N_{Di,e} \times 10^5$
1	201	29	189	147	42	76	97
2	203	29	183	143	40	79	101
3	402	29	216	179	37	94	113
4	404	24	252	209	43	81	97
				Average:	40	82	102

TABLE 4. DISPERSION NUMBERS FOR VARIOUS CENTRIFUGAL SEPARATORS WITH PADDLE MIXING

Reference	D, mm	ΔZ, mm	$\bar{r}$, mm	V, dm^3	Solvent Pair	ω, rad/s	Measured Capacity, dm^3/s	R	Continuous Phase[a]	$N_{Di} \times 10^4$
Roth (1969)	80	21	26.5	0.46	b	314	0.21	0.2	A	13
							0.19	0.5	O	12
							0.22	1	O	14
							0.25	2	O	15
							0.28	5	O	17
Bernstein et al. (1973A)	104	19.0	34.9	1.27	c	209	0.49	0.33	A	14
							0.35	0.5	O	10
							0.39	1	O	11
							0.39	2.5	O	11
						314	0.21	0.33	A	14
							0.16	0.5	O	11
							0.18	1	O	13
							0.19	2.5	O	14
Webster et al. (1969)	262	70.6	86.1	13.83	d	182.7	4.8	0.2	A	17
							3.4	0.5	O	12
							4.0	1	O	14
							5.0	2	O	18
							5.4	4	O	19

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[a] Our best estimate of which phase is continuous.

[b] A: 0.1 M HNO_3 and 1.0 M $NaNO_3$ in water.
O: 15% TBP in Shellsol T.

[c] A: 0.5 M HNO_3 in water.
O: 30% TBP in nDD.

[d] A: 0.5 M HNO_3 in water.
O: 30% TBP in "Ultrasene."

dispersion collected through the drain is typically a small fraction (5 to 10%) of the total flow through the contactor. For the 20-mm tests, settling tubes 16 mm in diameter were used with liquid heights of 50 to 100 mm. The dispersion collected usually represented all of the dispersion in the Couette mixing zone.

In the measurement of the dispersion number by centrifugal-settling flow tests, different procedures were needed. For the 94-mm and 262-mm units, which have air-controlled aqueous weirs, the dispersion band was shifted by changing the weir pressure until the band was located within the separating zone. As the throughput was increased at constant O/A ratio, the acceptable pressure range decreased until, at maximum throughput, only one pressure was acceptable and the dispersion band occupied the entire separating zone. From these data, N_{Di} was calculated. For the smaller 20-mm units, which do not have air-controlled weirs, the maximum throughput at various O/A ratios was measured and the mode of failure was noted. At low O/A ratios, the dispersion band will be close to the organic weir, and the mode of failure will be aqueous contamination in the organic phase. At high O/A ratios, the dispersion band will be close to the aqueous underflow, and the mode of failure will be organic contamination in the aqueous phase. At some intermediate O/A ratio, failure will occur by both modes simultaneously as the flow rate is increased. For this O/A ratio, the dispersion band completely fills the separating zone at maximum throughput so that the dispersion-band volume can be determined and, from this, the dispersion number can be calculated.

RESULTS

Effects of the operating variables of the Couette mixer on the dispersion number are shown in Figures 2 and 3. Varying throughput and rotor speed had no significant effect on N_{Di}. The O/A ratio also had no effect on N_{Di} except when the O/A ratio was varied enough to cause phase inversion. Phase continuity is important in determining the dispersion number with the aqueous-continuous value being about twice the organic-continuous value.

Dispersion-band thickness and acceleration within the separating zone were varied to find their effect on N_{Di}. The results, with N_{Di} plotted as a function of dispersion-band thickness, are shown in Figures 4 and 5 for aqueous- and organic-continuous operation, respectively. The N_{Di} values from continuous-flow centrifugal tests, which have accelerational forces over 100 times that of gravity, correlate well with N_{Di} values from batch gravity tests.

Couette mixer geometry was varied considerably with little effect on the dispersion number. First, the Couette gap has no significant effect on N_{Di} (Figure 6). Secondly, the rotor diameter does not affect N_{Di} (Figures 2 and 5). Thirdly, the liquid level in the Couette mixing zone, which varies with rotor speed, throughput, and vane geometry under the rotor, is considered. Since these variables, shown in Figures 2, 3, and 6 have little effect on N_{Di}, we conclude that the liquid height in the mixing zone has little effect on the dispersion number. Finally, the location and orientation of both feed ports were varied. The 94-mm Couette mixer was first run with tangential inlet ports 60 mm above the bottom of the rotor. Then the unit was run with perpendicular inlet ports entering more than twice as high in the Couette mixing zone, 160 mm above the bottom of the rotor. The dispersion number, as measured by contactor capacity, was unchanged.

Coalescence of the dispersed phase in the dispersion band was studied in more detail (Table 3). For these gravity-settling batch tests, the dispersion-band thickness and the fraction of dispersed phase in the remaining dispersion band were measured as a function of time, and the results are given in Figures 7 and 8, respectively. Figure 7 shows that the change in band thickness with time is linear for the first 75% of the coalescence in the dispersion band. Figure 8 shows that the deviation from this straight line occurs when the fraction of dispersed phase in the dispersion band reaches 0.75 ± 0.03. At this point, the remaining dispersion band is essentially the dense sub-layer described by Barnea and Mizrahi (1975).

DISCUSSION

These results show that, except for phase continuity, the degree of mixing in the Couette zone as measured by N_{Di} is essentially independent of operational parameters and mixer geometry. On this basis, the performance of the Couette mixer is similar to that reported by Ryon et al. (1959) for a flat-blade turbine mixer in a baffled tank. That process used di-ethylhexyl phosphoric acid dissolved in kerosene modified with tri-n-butyl phosphate (TBP) and a slightly acidic aqueous phase containing various metal ions. The dispersion numbers calculated from the data of Ryon et al. range from 0.006 to 0.0012 for studies in which the organic phase was continuous and from 0.0025 to 0.0035 for studies in which the aqueous phase was continuous. Otherwise, O/A values between 0.25 and 4 had no effect on N_{Di}. Also, changes in flow rate and power input (comparable to our changes in rotor speed) had no effect on N_{Di}. The effect of ΔZ on N_{Di} is given by $c = 0.2$ over the ΔZ range from 10 to 750 mm. The Couette mixing results reported here have c values from 0.0 to 0.2.

Data are also available which allow N_{Di} to be calculated for a third type of mixing system, small-volume paddle-mixers. These mixers are coupled with centrifugal settlers. Values of N_{Di}, calculated from the reported results, are listed in Table 4. In calculating the N_{Di} values, the dispersion band is assumed to fill the settling zone. If that is not the limiting factor, then N_{Di} is larger than shown. In particular, the data of Roth (1969) at R values of 0.5 and 2 include weir pressure measurements which indicate the dispersion band filled the separating-zone. These centrifugal settler results which are for solvent pairs like the ones used here show aqueous-continuous N_{Di} values at the low end of our values and organic-continuous N_{Di} values at the high end of our values. At any rate, the dispersions from a small-volume paddle-mixing zone seem to be roughly comparable to those from a Couette-mixing zone.

In this work, the degree of mixing or dispersion is evaluated using N_{Di}. A second method for evaluating the degree of mixing is to measure the mass-transfer efficiency when the Couette mixer is used in solvent extraction. Of particular interest is the transfer of uranium from aqueous nitric acid solutions to an organic phase of 30 vol. % TBP in *n*-dodecane (*n*DD). These tests have been made for the 104-mm mixer (Bernstein et al., 1973) and the extraction efficiency was found to be greater than 95%. Similar tests with the 20-mm and 94-mm mixers discussed here showed average extraction efficiencies of 94% and >98%, respectively. Thus, with respect to achieving good mass-transfer efficiency, the turbulent Couette mixer is quite effective.

Phase continuity is important to the dispersion characterization using N_{Di}. Figures 2 to 5 show that the ratio of the aqueous-continuous N_{Di} to the organic-continuous N_{Di} is 2.4 ± 0.4. This is in agreement with the earlier t_B measurements of Groenier (1968) for the same system, which give a ratio of 2.7. The factors that contribute to this change in N_{Di} upon phase inversion were not established. Some possible factors are differences in drop-size distributions for the different continuous phases, the difference in continuous-phase viscosity, and the difference in the electrical charge on the dispersed-phase droplets.

As a first approximation for a given pair of immiscible liquids, continuous-phase viscosity seems to be inversely proportional to the measured N_{Di}. This is true for the results reported here. This also seems to be true for the work of Groenier (1968) when aqueous-continuous and organic-continuous dispersions for a given pair of immiscible liquids are compared. However, in one case reported by Groenier (A: 0.1 *M* HNO_3 in water; O: 5% TBP in Amsco), N_{Di} is greater when that phase which is estimated to be the more viscous (the organic phase) is the continuous phase. In nonflow, gravity-settling dispersion bands which have coalesced to the point where they contain 75% or more of the dispersed phase (the dense layer), the theory of Leonard and Lemlich (1965) is shown by Allak and Jeffreys (1974) to give a flow rate, and hence N_{Di}, that is inversely proportional to viscosity. However, Figure 7 shows that the deviation in t_B, and hence N_{Di}, due to the appearance of this dense layer is only 15 to 25% of the total t_B for our system. For droplet velocity before the dense layer is formed, Eq. 12 shows that N_{Di} should vary only slightly with viscosity, that is, N_{Di} is proportional to $\mu^{-0.11}$. Additional study is needed to determine the dependence of N_{Di} on continuous-phase viscosity. As a rule of thumb, extractor capacity will generally be improved if the less viscous phase is made the continuous phase.

In this work, N_{Di} was found to be independent of the dispersion-band thickness. This independence is expressed as a zero value of the ΔZ exponent, c in Eq. 17. According to the analysis of Barnea and Mizrahi (1975), this zero c value indicates the rate of coalescence is very high. Thus, whenever droplets collide, they coalesce, and the rate of settling is controlled by the velocity of the growing droplets. At ΔZ's below 200 mm, the variability of gravity N_{Di} values increase markedly. This variability was also seen by Barnea and Mizrahi (1975) who, for that reason, limited their tests to values of ΔZ greater than 250 mm. This variability was not seen at high g values even though the small (20 mm) centrifugal contactor had a ΔZ of only 4.5 mm. Figures 4 and 5 show that data for various dispersion-band thicknesses, for flow and batch operation, and for gravity and centrifugal settlers all lie on a single curve as long as the same continuous phase is maintained. With this correlation, laboratory data can be used to design plant-size mixer-settlers or centrifugal contactors in a straight-forward manner.

No special effort was made to control room temperature during these tests. To see if this was appropriate, the dispersion number was measured as the temperature was increased from 24.9 to 29.0°C. From the results of Barnea and Mizrahi, a rough rule-of-thumb would be that the N_{Di} doubles as the temperature increases 20°C. Thus, for our 4.1°C rise in temperature, we expected roughly a $1.15\times$ increase in N_{Di}. With a 400-mm initial dispersion thickness for the gravity N_{Di} tests, N_{Di} actually went from 8.0×10^{-4} to 9.3×10^{-4}, a $1.16\times$ increase. Other tests in this series had initial dispersion thickness for the gravity N_{Di} tests less than 250 mm. The variability in N_{Di} measurements obscured any temperature effects. Thus, for tests where N_{Di} variability is low, that is for tests using a centrifugal separator or using a gravity separator with an initial dispersion thickness greater than 250 mm, temperature changes of a few degrees will have a small but measurable effect on the dispersion number.

The batch gravity-settling tests where ΔZ_t is measured as a function of time seem to provide a way to further characterize dispersions. For the first 75% of the ΔZ_t coalescence, the slope of ΔZ_t vs. t is linear (Figure 7) and the extrapolated dispersion number is seen in Table 3 to be independent of ΔZ. This $N_{Di,e}$ is then a measure of droplet size, velocity, and coalescence rate in the uniform dispersed state. This $N_{Di,e}$ is also equivalent to the reference time defined by Mizrahi and Barnea (1970). Table 3 also shows that the increase in time, Δt, above $t_{B,e}$ is a constant, which is 40 s for this system. This t, therefore, provides a measure of continuous-phase viscosity and drainage in the final dense layer which has a high concentration (>75%) of the dispersed phase. Using $N_{Di} = 0.0008$, $t_{B,e} = \Delta t = 40$ s to get t_B, and $\bar{a} = 9.81$ m/s^2 (Table 3), we calculate that $\Delta Z = 40$ mm. Thus, it appears that the region where gravity N_{Di} variability becomes pronounced ($2\times$) is the same as the region where $\Delta t > t_{B,e}$ and may be caused by Δt being greater than $t_{B,e}$. For design of solvent extractors, Figure 5 indicates that N_{Di} which uses t_B is more appropriate than $N_{Di,e}$ which uses $t_{B,e}$.

There is some evidence that the effect of ΔZ on N_{Di} as given by exponent c is not always zero for the immiscible liquids tested here. When N_{Di} values were determined by gravity-settling batch tests, N_{Di} appears to depend slightly on ΔZ. This trend is seen in both Figure 5 and Table 3. In Table 3, the dependence of N_{Di} on ΔZ is given by $c = 0.18$.

In solvent extraction, many solvent pairs have been used. It is of interest to know what range of N_{Di} values can be expected. Reviewing the data of Barnea and Mizrahi (1975), and of Rodger et al. (1956) and Rodger (1956), we calculate values of N_{Di} from 0.0001 to 0.020, with most values falling in the 0.0005 to 0.004 range. As noted above, the results summarized in Barnea and Mizrahi (1975) show that N_{Di} usually increases as temperature increases. One exception to this rule was found. It may be significant that this exception, and two other exceptional cases, where N_{Di} decreased as the degree of mixing was increased, all had high-c values above 0.25, that is, $y > 4$. In these high-c systems, the rate of droplet coalescence should be lower, so that it would take longer to reach a steady-state balance between droplet breakup and droplet coalescence and the systems would be more sensitive to mixing intensity. The system with the lowest N_{Di} value (0.0001) was one of the systems sensitive to mixing intensity. This N_{Di} value is based on the data of Howarth (1967), as recalculated by Barnea and Mizrahi (1975). That c values are generally low, below 0.25, as reported in the literature as well as found here, is an indirect indication that resistance to droplet coalescence is not significant for solvent pairs normally used in solvent extraction. In fact, having a low-c value, that is, a low dependence of N_{Di} on settling length, may be an important characteristic for a solvent pair to have if they are to be useful in solvent extraction processes.

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NOTATION

A = cross-sectional area of dispersion settling zone, m^2
a = accelerational field acting on a dispersion settling zone, m/s^2
$\bar{a}$ = average a in a centrifugal field, Eq. 4, m/s^2
C = droplet drag coefficient, dimensionless
c = exponent used to correlate ΔZ with N_{Di}, Eq. 17, dimensionless
D = rotor diameter, m
d = droplet diameter, m
d_c = critical droplet diameter as defined by Klee and Treybal (1956), m
g = gravitational acceleration, m/s^2
ΔH_g = gap height (clearance) between vanes below the rotor and the bottom of the rotor, m
ΔH_v = height of the bottom vanes below the rotor, m
i = parameter dependent on droplet Reynolds number, dimensionless
j = parameter dependent on the rate of droplet coalescence, dimensionless
L_c = length of Couette mixing zone, m
N_{Di} = dispersion number, Eq. 3, dimensionless
$N_{Di,e}$ = N_{Di} where $t_{B,e}$ replaces t_B, dimensionless
$N_{Re,d}$ = droplet Reynolds number = $dU\rho_c/\mu_c$, dimensionless
n = number of bottom vanes under the rotor, dimensionless
q = flow rate through or capacity of a centrifugal contactor or a mixer settler, m^3/s
R = O/A ratio, dimensionless
R.T. = room temperature
r = radius out from centerline of rotor, m
$\bar{r}$ = radius which represents the volume-average accelerational force on the dispersion in the separating zone of a rotor, Eq. 5, m
$r_{H,i}$ = inside radius of the rotor housing, m
$r_{R,o}$ = outside radius of the rotor, m
r_o = inner radius of the separating zone inside the rotor, physical organic weir radius, m
r_u = outer radius of the separating zone inside the rotor, aqueous underflow radius, m
Δr_c = $r_{H,i} - r_{R,o}$ = Couette mixing zone gap, m
T = temperature of solvent pair, °C or °K
t = time elapsed since mixing was stopped and the dispersion started to coalesce, s
t_B = time for dispersion to break, s
$t_{B,e}$ = extrapolated t_B value using linear portion of ΔZ_t vs. t curve on Figure 7, s
t_R = residence time in the separating zone, s
t_s = settling time for droplet in the separating zone, s
Δt = $t_B - t_{B,e}$, s
U = terminal velocity of the droplet, m/s
V = volume of the dispersion band in the separating zone, m^3
y = exponent on flow rate per unit area, Eq. 13, dimensionless
ΔZ = thickness of the separating zone actually used by the coalescing dispersion band in a flowing system or the initial dispersion depth in a batch system, m
ΔZ_t = thickness of the remaining dispersion band in a batch system at time t, note that $\Delta Z_0 = \Delta Z$, m

Greek Letters

ϵ = fraction of dispersed phase in the dispersion band, dimensionless
μ = viscosity, Pa · s
μ_c = continuous-phase viscosity, Pa · s
ρ = density, kg/m^3
ρ_c = continuous-phase density, kg/m^3
ρ_d = dispersed-phase density, kg/m^3
$\Delta\rho$ = $|\rho_c - \rho_d|$, kg/m^3
σ = interfacial tension, N/m
ω = rotor velocity, rad/s

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