N = impeller speed, sec.$^{-1}$
N_{Re} = ND^2/ν = Reynolds number
N_{We} = $L^3N^2\rho/\sigma$ = Weber number
n_i = number of drops in the i^{th} size interval
$P(D)$ = probability that a drop of size D exists
T = tank diameter, cm.

Greek Letters

α = constant in Equation (9)
ε = turbulent energy per unit mass, defined by Equation (7), sq.cm./sec.^{2}
ϵ = local energy dissipation per unit mass, sq.cm./sec.^{3}
$\bar{\epsilon}$ = average power input per unit mass, sq.cm./sec.^{3}
η = dissipation microscale, cm.
ν = kinematic viscosity of continuous phase, sq.cm./sec.^{1}
ρ = density of continuous phase, g./cc.
σ = interfacial tension between phases, g./sec.^{2}
ϕ = volume fraction of dispersed phase

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Drop Size Distributions in Strongly Coalescing Agitated Liquid-Liquid Systems

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Emulsion drop size distributions have been measured at various locations in a turbine mixer for the methyl isobutyl ketone-salt water system. The drop sizes are strongly dependent on the sampling position, being smallest near the impeller tip and largest at the bottom of the mixing tank. The variation of drop diameter with impeller speed has been studied and indicates that droplet breakup predominates near the impeller, whereas the coalescence of emulsion droplets can be controlling in other locations.

Many engineering operations depend on effective mass transport across liquid-liquid interfaces. The transport is, of course, strongly affected by the amount of interfacial area present in the vessel. The interfacial area is directly related to the distribution of drop sizes produced in the emulsion.

In a previous paper (7) the use of an electronic particle counter was described for the determination of complete drop size distributions in dilute (low fraction dispersed phase) agitated liquid-liquid systems. This method has been extended for use with more concentrated systems, and in the present work a mixture of 25% methyl isobutyl ketone (MIBK) and 75% salt water was emulsified in a turbine mixer. The emulsion was sampled at various locations in the mixing tank, and drop size distributions determined.

The methods of isotropic turbulence provide tools for the prediction of drop sizes in systems in which either the process of dispersion or prevention of coalescence acts on a given fluid element. Measurements have been made to indicate whether these two processes can simultaneously control the drop sizes produced in different locations in a mixer.

EXPERIMENTAL WORK

Agitator and Materials

The mixing vessel was a fully baffled Pyrex tank, 8¾ in. in diameter, and filled with the liquid-liquid mixture to a height equal to the vessel diameter. A 2½-in. diameter turbine impeller with six flat blades was driven by a variable speed motor and was located 3 in. off the vessel bottom. A cover plate prevented air from being incorporated in the emulsion at high mixing speeds. The equipment was essentially that described in an earlier paper (7), a more complete description of the mixing apparatus being offered in that work.

Different liquid-liquid systems were screened before the system MIBK + 1% sodium chloride in water was adopted for intensive study. The effects of dispersion and coalescence were quite apparent in this system for the particular mixing geometry employed. The physical properties of the two liquid phases were measured at 20 ± 0.5°C. and are as follows:

Liquid	Density, g./cc.	Viscosity, centipoise
Methyl isobutyl ketone	0.80	0.59
1% sodium chloride in water	1.005	0.99

These properties, as well as the interfacial tension, were measured at the end of a high speed mixing run. The interfacial tension was 9.3 dynes/cm.

Particle Size Analysis

Drop size distributions were obtained for samples of the emulsion using a Coulter Counter Model B (Coulter Electronics, Chicago). Although the counter was originally developed to count blood cells, it has been extensively used to size powders and to a lesser extent, emulsions. Figure 1 presents the essential features of the counter. After uniform mixing, a sample of emulsion is withdrawn from the mixing vessel through a sampling loop and immediately diluted to a phase volume of 0.05 to 0.5% in a mixture of additional salt water and glycerine. This dilute emulsion is then transferred to a beaker associated with the particle counter. The dilution and stabilization with glycerine retard coalescence of particles during the counting period, this being especially necessary in this very rapidly coalescing system. The exact dilution and amount of stabilizer are determined by trial and error for each sample. The stopcock is then opened and a controlled vacuum system pulls emulsion from the beaker into the aperture tube through a small aperture. During the passage of the emulsion particles through the aperture, an electric current passing through the continuous salt water phase between two electrodes is interrupted. This produces voltage pulses, the amplitudes of which are approximately proportional to the volumes of the emulsion particles. These pulses are amplified, scaled, counted, and displayed both on a cathode ray tube and a digital register.

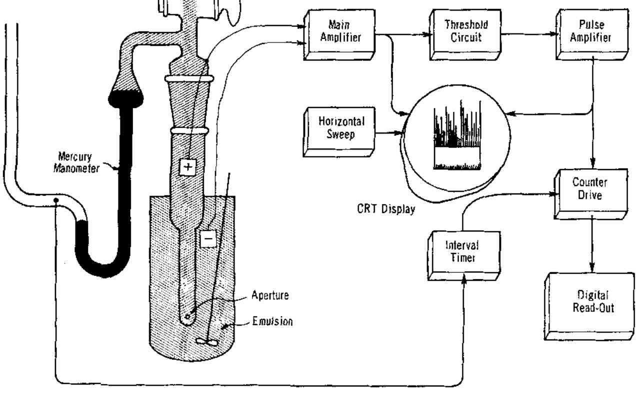

Fig. 1. Detail of particle counter.

In practice, one counts the number of particles larger than a particular size, using a threshold circuit to prevent counting smaller particles. The setting of the threshold is then changed to allow counting above a new size. In this way a cumulative distribution of drop sizes is obtained. An interval timer (Coulter Model EE) is used to ensure that the same emulsion volume is counted each time.

In this work, an aperture of 560 μ diameter was used, allowing an accurate analysis for particles in the range 25 to 275μ. Calibration of the counter and aperture was made with a corn pollen (obtained from Hollister-Stier Laboratories, Dallas) of 86 μ mean diameter.

One basic assumption in the interpretation of the counts is, of course, that only one emulsion particle goes through the aperture at a time; that is, each pulse corresponds to only one particle. The emulsion must be diluted in the beaker to satisfy this condition. The instrument therefore has the disadvantage of not being capable of counting in concentrated emulsions, but in many cases dilution does not affect the drop size distribution (7).

DROPLET BREAKUP AND COALESCENCE

Dispersion

Equations have been derived (6, 7) for the dispersion of emulsion droplets in regions that are locally isotropic. Two mechanisms are apparent: one in which inertial effects predominate in the breakup of a drop, and another in which viscous forces cause breakup. The resulting equations are

$$d_{\max} = k_1 \sigma^{3/5} \rho_c^{-3/5} N^{-6/5} D^{-4/5} \qquad (1)$$

for breakup by inertial effects, and

$$d_{\max} = k_2 \sigma \nu_c^{1/2} \mu_c^{-1} N^{-3/2} D^{-1} f(\mu_d/\mu_c) \qquad (2)$$

for breakup due to viscous shear. Various investigators (7 to 9) have found that Equation (1) is in good accord with experimental data.

It is usually believed (6) that Equations (1) and (2) should apply to droplets larger and smaller than the Kolmogoroff length, respectively. The Kolmogoroff length is defined as

$$\eta \equiv (\nu_c^3/\epsilon)^{1/4} \qquad (3)$$

However Vermeulen's (9) data on gas-liquid dispersions seem to obey Equation (2) despite the fact that the drops are larger than the Kolmogoroff length. No previous investigator has correlated experimental results on a liquid-liquid system with an expression similar to Equation (2).

Coalescence

Work by Deryaguin (3) and others has indicated that the coalescence phenomenon is well described by a force parameter F representing the force of interaction between two particles. A critical energy input will result when the turbulent forces tending to separate two particles just equal this force of attraction or coalescence.

In the region of inertial effects (large drop diameter) then

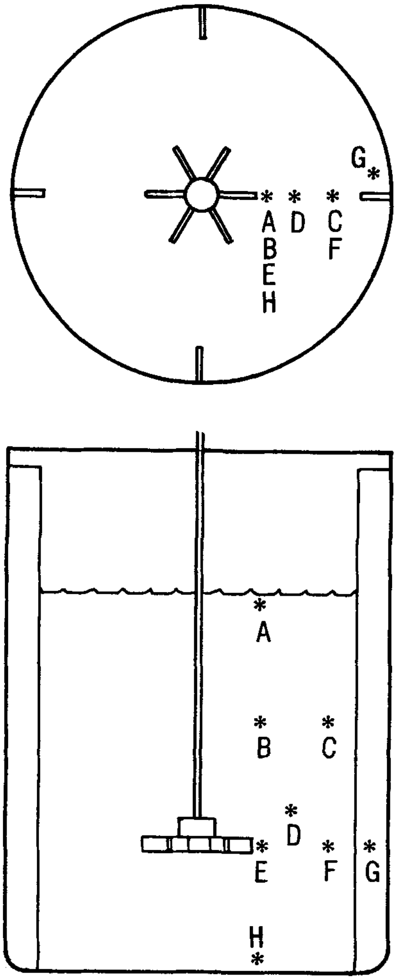

Fig. 2. Position of sampling points.

$$\rho_c \, \overline{u^2} \, d_{\min}^2 = F \tag{4}$$

where $\overline{u^2}$ is the mean square velocity difference and $d_{\min}$ is the diameter of the smallest particle whose coalescence is retarded by turbulence. From dimensional analysis (*6*, *7*)

$$\overline{u^2} = k_3 \epsilon^{2/3} \, d_{\min}^{2/3} \tag{5}$$

Therefore

$$d_{\min} = k_4 F^{3/8} \, \rho_c^{-3/8} \, \epsilon^{-1/4} \tag{6}$$

For a fully baffled turbine mixer ϵ = constant $\cdot (N^3 D^2)$. Assume that the energy dissipation in the coalescing region of interest is proportional to this total energy dissipation; then

$$d_{\min} = k_4 F^{3/8} \, \rho_c^{-3/8} \, N^{-3/4} \, D^{-1/2} \tag{7}$$

The equation has also been derived by Shinnar (*6*).

In the region of viscous shear, at critical conditions

$$\mu_c \, \overline{\nabla u} \, d_{\min}^2 = F \tag{8}$$

where $\overline{\nabla u}$ is the local velocity gradient. From dimensional analysis (*7*)

$$\overline{\nabla u} = k_5 \epsilon^{1/2} \, \nu_c^{-1/2} \tag{9}$$

The final result for a baffled turbine is

$$d_{\min} = k_6 F^{1/2} \, \nu_c^{1/4} \, \mu_c^{-1/2} \, N^{-3/4} \, D^{-1/2} \tag{10}$$

As pointed out by Shinnar (*6*) the results of Rodger et al. (*5*) for geometrically similar systems are well correlated by Equation (7). For the concentrated emulsions used by Rodger it was thus concluded that coalescence was more important than dispersion. It would be quite difficult to distinguish between Equation (7) for the inertial region and Equation (10) for the viscous region from available data.

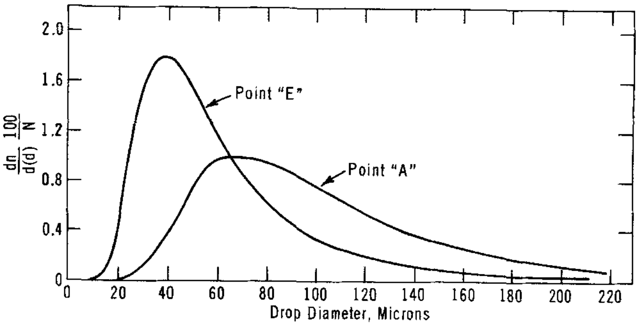

Fig. 3. Drop size distributions at two sampling points (1,000 rev./min, $\phi = 0.25$).

RESULTS

Drop Size vs. Location in Mixing Vessel

Work by Vanderveen (*8*) and Calderbank (*1*) has shown that drop sizes may vary throughout the mixer for certain systems. Vanderveen measured average drop diameters in liquiid-liquid systems along a vertical axis near the impeller tip and found that drop sizes increased as the probe approached the liquid surface. Calderbank found strong variations in bubble size for gas-liquid dispersions at various tank locations.

Vanderveen's results indicate that the droplets are broken up near the impeller and coalesce along a circulation path until they are returned to the impeller. Recent data by Cutter (*2*) show that the intensity of turbulence is much higher near the impeller than at other tank locations. Hillestad (*4*) has recently presented a correlation for coalescence rates in agitated systems, and has found that a model based on breakup near the impeller and continuous coalescence along a circulation path correlates his data quite well.

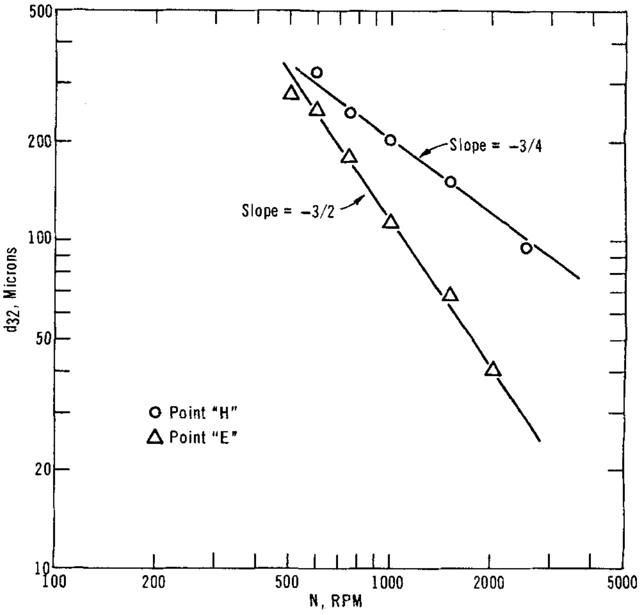

Fig. 4. Effect of impeller speed on average drop diameter (ϕ = 0.25).

TABLE 1. MEAN DROP DIAMETERS AT VARIOUS LOCATIONS

$N = 1{,}000$ rev./min., $\phi = 0.25$

Position	d_{32}, μ	Std. dev. in. d_{32}, μ
A	169	8
B	144	5
C	136	6
D	153	14
E	119	3
F	131	5
G	162	9
H	204	13

In the present work samples of the emulsion were extracted from the vessel at a number of points which are shown in Figure 2. These samples were sized and counted and a cumulative distribution function was determined for each sample. These distribution functions were fitted to high-order polynomials and differentiated to yield numerical distribution functions. These functions are shown in Figure 3 for two sampling points, one at the impeller tip and another near the liquid surface. These curves are for a volume fraction MIBK of 0.25 and a mixer speed of 1,000 rev./min., all measurements being made at 20°C. It is evident that very large differences in drop size distributions are apparent in these locations. A large number of particles have coalesced to form larger particles between the point of initial dispersion (point *E*) and the upper surface (point *A*). The distribution functions themselves are more complicated than those found earlier (7) for breakup in dilute emulsions, especially for sampling positions distant from the impeller.

One parameter of interest which can readily be obtained from the particle counts is the Sauter mean drop diameter d_{32}, where

$$d_{32} \equiv \frac{\Sigma n_i d_i^3}{\Sigma n_i d_i^2} \tag{11}$$

This mean diameter is related to the surface area per unit volume and the volume fraction dispersed phase through the equation

$$d_{32} = \frac{6\phi}{A} \tag{12}$$

The values of d_{32} at various sampling points are given in Table 1. The standard deviations of several determinations are also indicated.

Dispersion Near Impeller Tip

The emulsion was sampled at point *E* near the impeller tip at various impeller speeds and the results are shown in Figure 4.* The samples were extracted after the impeller speed had been constant for over 1 hr. On this log-log plot the data are quite well correlated by a line of slope $-3/2$. This corresponds to the dependence predicted by Equation (2) if the values of d_{32} are proportional to $d_{\max}$ (see reference 7). This result is unexpected since the drops produced are significantly larger than the Kolmogoroff length, which is estimated (7) to be from 5 to 10 μ, depending on the impeller speed. Evidently viscous effects are controlling the breakup despite the large drop size.

Regions of Coalescence

If the drop circulation model is correct, regions in which the drop diameters are much larger than those produced at the impeller tip are undergoing coalescence to the essential exclusion of additional dispersion. In these regions the coalescence process may be controlling in the sense that the turbulent forces would be retarding coalescence of the dispersed phase droplets. In Figure 4 the results of sampling at the bottom of the mixing tank (point *H*) are shown. On this log-log plot a slope of $-3/4$ correlates the data, as would be expected from either Equation (7) or (9) if the values of d_{32} are considered to be approximately proportional to $d_{\min}$. No distinction between these equations is possible since the same speed dependence is predicted.

CONCLUSIONS

Significant changes in drop diameter distributions throughout a mixing vessel are apparent in liquid-liquid systems that exhibit strong coalescence. The methyl isobutyl ketone–salt water system studied exhibits an unexpected dependence of drop diameter on impeller speed in the dispersion region near the impeller. Regions in the mixing tank are apparent in which the breakup of emulsion droplets determines the mean drop size produced; in other locations the coalescence process controls drop size.

NOTATION

A = surface area per unit volume
d = drop diameter
D = impeller diameter
f = function
F = force parameter
k = constant
n = number of drops of a particular size
N = total number of drops, impeller speed
u = velocity

Greek Letters

ϵ = local rate of energy dissipation
η = Kolmogoroff length
μ = viscosity
ν = kinematic viscosity
ρ = density
σ = interfacial tension
ϕ = volume fraction dispersed phase

Subscripts

c = continuous phase
d = dispersed phase
max = maximum stable size
min = minimum stable size

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