Characteristics of Inclusions in the Dispersed Phase of Liquid-Liquid Suspensions

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The classical emulsion is made up of drops of one liquid dispersed in a containing liquid. Under certain circumstances, however, some of the containing phase may form drops within the drops of the dispersed liquid, giving rise to a structure known as a double-multiple emulsion. This study was an investigation of the hydrodynamic formation of these structures.

Double-multiple emulsions were produced by using both transient and steady state liquid injection, with a cylindrical jet configuration. Analysis of the spray was by means of high-speed photography.

The distribution of the large drops and that of the included drops were both found to be represented satisfactorily by a log-normal probability function. A simplified model based on the use of nozzle parameters satisfactorily correlated percent included area and volume as a function of Reynolds number and Weber number. Large dispersed phase drops contained proportionally many more inclusions than did the smaller sizes.

The mechanism of inclusion formation was found to involve the drawing out of a ligament or sheet from the flowing jet, followed by the recoalescence of the free end of this ligament or sheet with the main jet body, entraining in the process a portion of the containing phase. Thus, the inclusions predate the formation of the drops of the dispersed phase from the jet disruption.

The classical emulsion is composed of a number of minute drops of one liquid within a containing phase of another liquid. The two liquids are commonly referred to as the *dispersed phase* and the *continuous phase*, respectively. In the simplest case we have the situation depicted in Figure 1, where there is a single dispersed phase, and the containing phase is truly continuous in the sense that any two points in the containing phase can be joined by a line lying entirely within that phase.

Under some circumstances, however, it is possible to get some of the containing phase within the drops of the other phase, as shown in Figure 2, making the containing phase no longer continuous. Here the terms *continuous phase* and *dispersed phase* lose any meaning as applied to the resultant emulsion. (They will, of course, have some relevance in the sense that one normally creates an emulsion by adding what may be termed the *dispersed phase.*) Emulsion structures which lack a continuous phase are normally referred to as *multiple emulsions.*

Multiple emulsion structures can be created in surprising complexity; for example, Clayton (2) cites an example of a quinque-multiple emulsion, shown schematically in Figure 3. The multiplicity or level of the multiple emulsion might be defined as the maximum of the minimum number of phase boundaries it is necessary to cross in going from any point (x_1, y_1, z_1) in the outermost phase to any other point (x_2, y_2, z_2) of the system. Thus, in Figure 3 we can see that it is necessary to cross five phase boundaries in going from point 1 to point 2. In the present study, we are concerned with multiple emulsions of the double-multiple type shown in Figure 2.

To avoid confusion, it should be pointed out that there is often reference in the literature to dual emulsions. This usage usually refers to pairs of liquids which, through the use of different emulsifying agents, will form emulsions of both oil in water and water in oil types and will frequently invert from one type to the other upon addition of a suitable reagent. These are conjugate systems but not coexisting systems; that is, at any given time, only a water in oil or an oil in water emulsion is present. Obviously, a pair of liquids must have the dual property in order to form stable double-multiple emulsions.

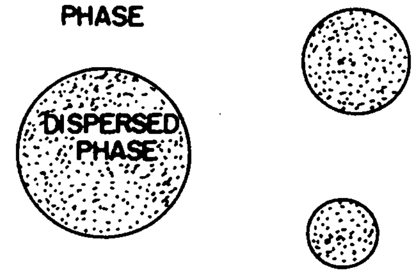

Fig. 1. Simple emulsion.

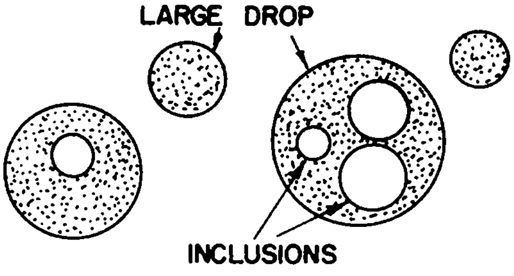

Fig. 2. Double-multiple emulsion.

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In the double-multiple emulsion, one has essentially two classes of drops (see Figure 2). The drops contained within the large drops, that is, the drops of the same composition as the external phase, will here be referred to throughout as the *inclusions;* the larger drops which are of composition opposite that of the external phase will be referred to as the *large drops.*

The creation of multiple emulsions in a commercial process is of interest mainly because of two properties. First, the formation of a multiple emulsion provides a greatly increased surface area for mass transfer between two liquid phases. Second, the formation of inclusions of the external phase within drops of the other phase interrupts the continuity of the external phase and prevents mixing.

Previous workers have seldom observed multiple emulsions in commercial equipment. The work here indicates that this is probably not because such emulsions do not exist, but rather that their stability is usually such that they disappear before they are observed. Their effects, therefore, are probably only important for systems where mass transfer is very rapid. However, in these systems significant mass transfer may occur across the interfacial area internal to the drops.

PREVIOUS WORK

Multiple emulsions as a class are not new. The early literature is primarily concerned with their production as an inversion phenomenon, for example, through the addition of the disperse phase or a suitable reagent to a simple emulsion, causing the structure to invert from O/W to W/O or vice versa, in the process trapping some of the original structure in the inverted emulsion. Later studies noted that there seemed to be some hydrodynamic factors involved as well; for example, the same effect could at times be produced by shaking or stirring.

One of the earlier observations with regard to multiple emulsions is made by C. V. Boys in his classic treatise "Soap Bubbles—Their Colours and the Forces Which Mould Them" (New York: Young, 1890). Boys notes that the liquid pairs petroleum and water and orthotoluidine and water will produce multiple emulsions. Boys' work is one of the earliest which makes reference to liquid-liquid multiple emulsions.

In recent years, there have been two articles which make observations with regard to multiple emulsions that apparently have been produced hydrodynamically. The first of these is an article by Pavloshenko and Yanishevskii (3) on interfacial area of mechanically stirred liquids.

Pavloshenko and Yanishevskii were concerned with the prediction of interfacial surface area created by agitation of two liquid phases in a container with a mechanical stirrer. They observed multiple emulsions in the system machine oil in water and show a photograph similar to some of the ones taken in conjunction with this research. They also note observation of multiple emulsions in the medicinal petrolatum in water system.

The second publication is one of R. H. Boll (*1*). Boll, like Pavloshenko and Yanishevskii, studied interfacial area of liquid-liquid dispersions, but rather than creating the dispersion by mechanical agitation, he used a conical spray nozzle and transient injection. Boll observed multiple emulsions in the systems SAE 10 motor oil and water and kerosene and water.

Both of these articles noted observation of multiple emulsions only when one or both members of the liquid pair was highly viscous. As will become evident in the following presentation, this is a stability phenomenon.

EXPERIMENTAL EQUIPMENT AND PROCEDURE

The photographic technique (5) used in the course of this research consists of taking an actual photograph of the spray droplets with high-speed still-picture photographic equipment. Double-exposure pictures are taken as well as single exposures. A known, very short, time delay is used between the two exposures of the double-exposure shots. The single exposure photographs are then counted, that is, the number of drops in each of a selected series of size classes is determined. This gives an instantaneous or spatial drop distribution. The double-exposure photographs are then measured to determine the distance between successive images (and thus the velocity) of each class of drops. By weighting the spatial distribution with the drop velocities, one can obtain the desired temporal spray distribution.

This process has the disadvantage of judgment involved in the counting process. It is, however, the only method applicable to multiple emulsion work at this time, since only by direct visual observation it is possible to discriminate between the large drops and the inclusions.

Figure (4) shows the physical relationship of the experimental equipment. This investigation was conducted by using cylindrical jets from hypodermic needles. The photolights gave a flash duration of the order of 1 to 2 μsec., with a range of controlled delays between flashes of about 10 to 1,500 μsec. The camera used for negatives for drop counting gave a magni-

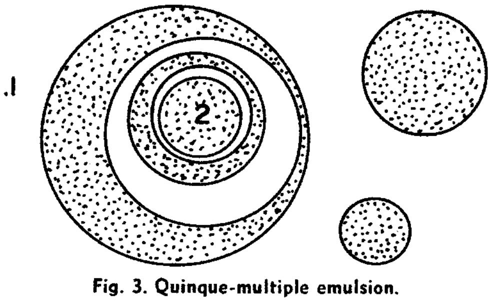

Fig. 3. Quinque-multiple emulsion.

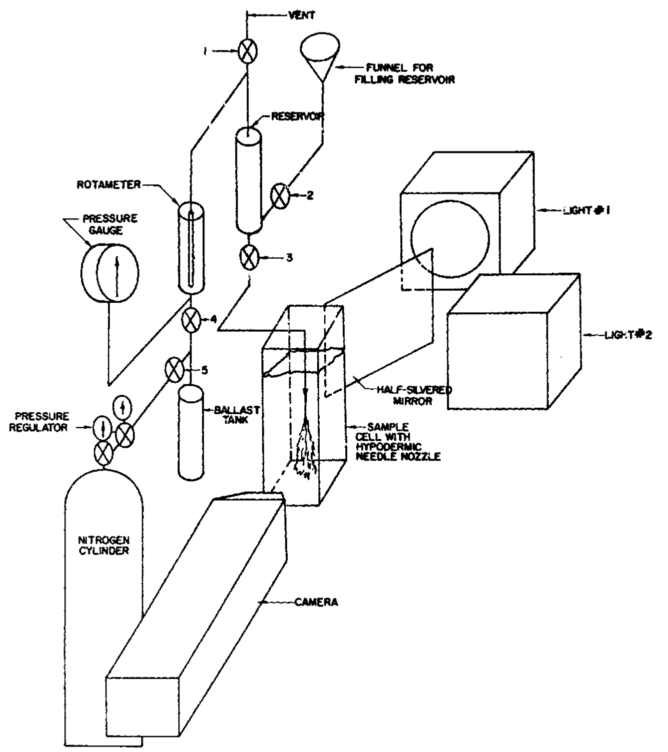

Fig. 4. Schematic diagram of experimental equipment.

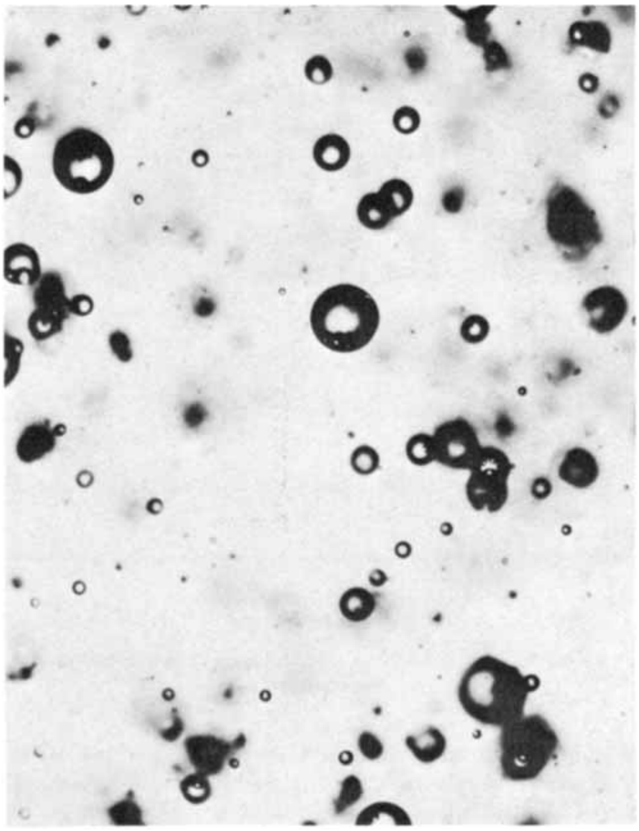

Fig. 5. Print from typical single-flash photo.

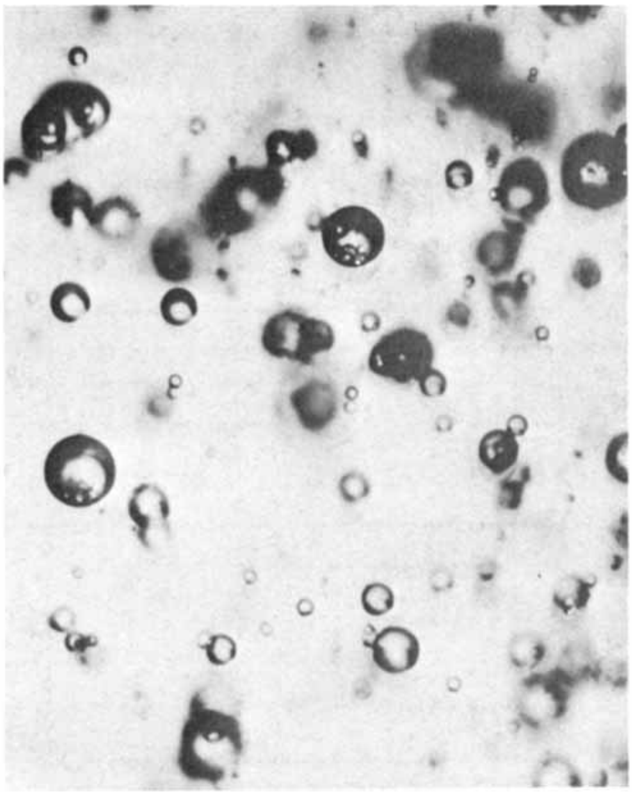

Fig. 6. Print from typical double-flash photo.

fication of 10 diam., and the negatives were examined by using an additional 10-diam. magnification for a total of 100 diam.

Typical single and double exposure photos are shown in Figures 5 and 6.

COUNTED DATA[*]

By counting the single-exposure photographs, one obtains the distribution of large drops within a preselected series of size ranges, and the distribution of inclusions within another preselected series of size ranges according to the diameter of the parent drop.

The counted data can be depicted as shown in Figure 7. For M preselected size ranges, we can characterize the diameter of the large drops by the mean diameter of the range, denoted by D_i ($1 \leqq i \leqq M$, i = integer). Similarly, we can preselect N size ranges for the inclusions and characterize them by their mean diameters d_j ($1 \leqq j \leqq N$, j = integer). Associated with the vector D_i there will be two vectors obtained from the drop counting process. The first is the distance vector, which we denote by l_i, and which represents the distance traveled by drops in the respective size range. Coupled with knowledge of the time delay used, this vector will yield our velocities. The second vector represents the number of drops y_i of diameter D_i which we observe in counting the single-exposure photographs.

We also obtain a matrix of values x_{ij}, where x_{ij} denotes the number of inclusions counted of size d_j within a parent drop of size D_i. These data, coupled with data on flow rate, interfacial tension, etc., were fed to a computer program which carried out the routine calculation.

All counted data were taken on the carbon tetrachloride-water system. Three nozzle diameters were used: 0.420, 0.642, and 1.042 mm. Liquid velocities through the nozzle ranged from 39 to 902 cm./sec., and interfacial tension was run at levels of 32.0 and 11.7 dynes/cm. Density ratio was varied by interchanging sprayed and receiving fluid, with levels of 0.63 and 1.60 resulting. Viscosity ratio was about 1.0 for the counted data; however, work done on mechanism was at a viscosity ratio of receiving fluid to sprayed fluid of about 1,000, with the same mechanism operative.

From the counted data, it was possible to study two things. First, it was possible to determine a probability distribution function which would adequately represent the distribution of inclusions and of large drops. It was then possible to correlate certain parameters of the process against the independent variables.

DETERMINATION OF PROBABILITY DENSITY FUNCTION

There have been many probability density functions proposed for use in spray research. Most of these are some specialization of a function of the type (4)

$$f(z) = \alpha z^{\beta} e^{-\gamma z^{\delta}}$$

The decision as to which distribution to use must usually be made on purely pragmatic grounds; it is occasionally possible to justify a given distribution on theoretical grounds but almost always by post facto reasoning.

We considered here three density functions common in spray work:

The log normal distribution:

$$f(\omega) \frac{1}{\sqrt{2\pi}} e^{-\omega^2/2}$$

The Rosin-Rammler distribution:

$$f(z) = bnz^{n-1} e^{-bz^n}$$

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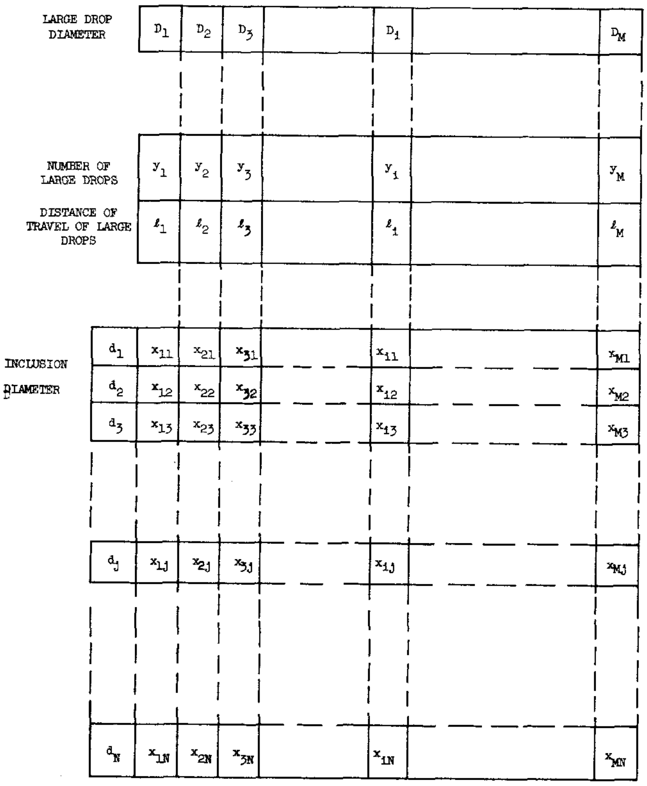
[*] All original data may be found in the doctoral dissertation of D. P. Kessler which may be obtained from University Microfilms, Ann Arbor, Michigan.



	D_1	D_2	D_3	D_i	D_M
LARGE DROP DIAMETER	D_1	D_2	D_3	D_i	D_M
NUMBER OF LARGE DROPS	y_1	y_2	y_3	y_i	y_M
DISTANCE OF TRAVEL OF LARGE DROPS	l_1	l_2	l_3	l_i	l_M
INCLUSION DIAMETER d_1	x_{11}	x_{21}	x_{31}	x_{i1}	x_{M1}
d_2	x_{12}	x_{22}	x_{32}	x_{i2}	x_{M2}
d_3	x_{13}	x_{23}	x_{33}	x_{i3}	x_{M3}
d_j	x_{1j}	x_{2j}	x_{3j}	x_{ij}	x_{Mj}
d_N	x_{1N}	x_{2N}	x_{3N}	x_{iN}	x_{MN}

Fig. 7. Schematic diagram of counted data.

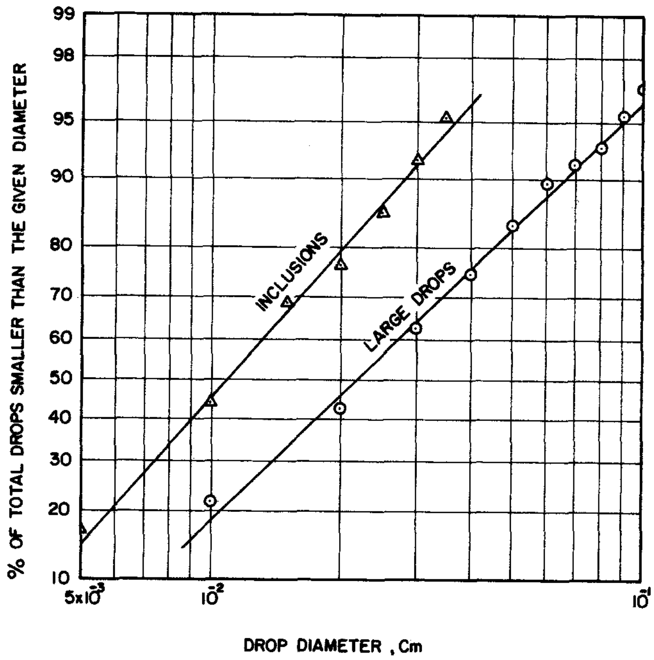


Fig. 8. Typical fit of log-normal function to large drop and inclusion distributions.

The Nukiyama-Tanasawa distribution:

$$f(z) = az^2 e^{-bz^n}$$

All three of these density functions are integrable as special cases of the incomplete gamma function:

$$\Gamma_\alpha(l) = \int_0^\alpha t^{l-1} e^{-t}\, dt$$

This is a tabulated function available in standard references.

The data can be tested for fit to the log-normal case by plotting on log probability paper the estimates of the cumulative probability distribution function $F(z)$. These estimates may be obtained from the counted data as

$$\hat{F}(D_m) = \frac{\sum_{i=1}^{m} y_i l_i}{\sum_{i=1}^{M} y_i l_i} \quad (1 \leqq m \leqq M)$$

and

$$\hat{F}(d_n) = \frac{\sum_{i=1}^{M} \sum_{j=1}^{n} x_{ij}\, l_j}{\sum_{i=1}^{M} \sum_{j=1}^{N} x_{ij}\, l_i} \quad (1 \leqq n \leqq N)$$

Plotting the estimates of $F(z)$ vs. D_i and d_j, respectively, should yield a straight line if a fit to the log-normal distribution is obtained. A typical set of data is shown in Figure 8.

Similar techniques may be used to test the fit of the data to the Rosin-Rammler and Nukiyama-Tanasawa functions. Fits in each of these cases were poorer than with the log-normal distribution. Since the two more sophisticated functions show no better fit to the experimental data than the log-normal function, there is no

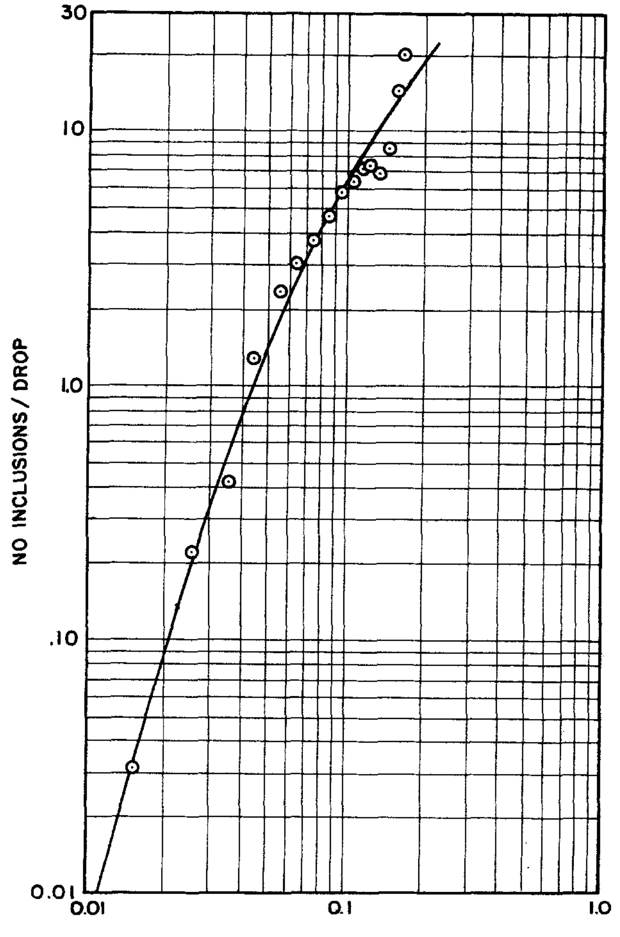


Fig. 9. Number of inclusions per drop as a function of large drop diameter.

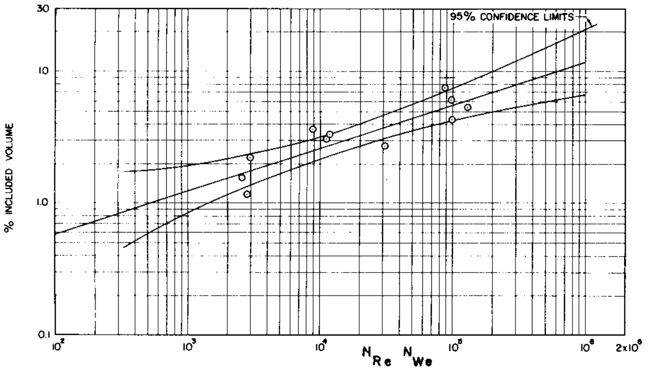


Fig. 10. Percent included volume as a function of $N_{Re} \times N_{We}$.

justification for using the more complicated models on the basis of this work.

CORRELATION OF MULTIPLE EMULSION PARAMETERS

The most immediate observation from considering the relationship of the distribution of inclusions to that of the large drops is that the large drops contain a much higher number of inclusions than the smaller drops. This can be seen graphically in Figure 9. The number of inclusions per drop is of the order of 10 to 20 in the largest diameter drops but less than 1 in the smaller size ranges. This observation fits well with the proposed mechanism discussed below.

The number of inclusions per drop can be seen to be approximately proportional to the volume of the large drop, that is, to the cube of the large drop diameter. The line in fact is not straight but deviates toward the upper end. This may well be caused by the obscuring of some of the inclusions by others nearer in the field of view, an effect impossible to avoid with the photographic method used.

An attempt was made to correlate the number of inclusions per drop with Reynolds number and Weber number without success. Apparently the probability of an inclusion being trapped inside a drop is mainly proportional to the relative volume of that drop. This is reasonable under the proposed mechanism, since the mean inclusion diameter is relatively small compared with the mean large drop diameter.

The data plotted in Figure 9 represent about 2,500 large drops and 1,500 inclusions from a 0.00642-cm. nozzle at a variety of combinations of density ratio, interfacial tension, and velocity.

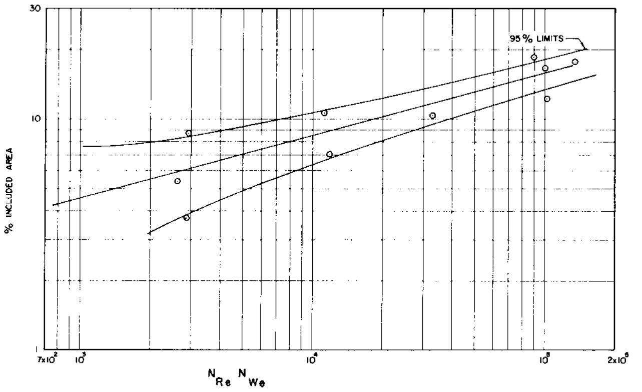


Fig. 11. Percent included area as a function of $N_{Re} \times N_{We}$.

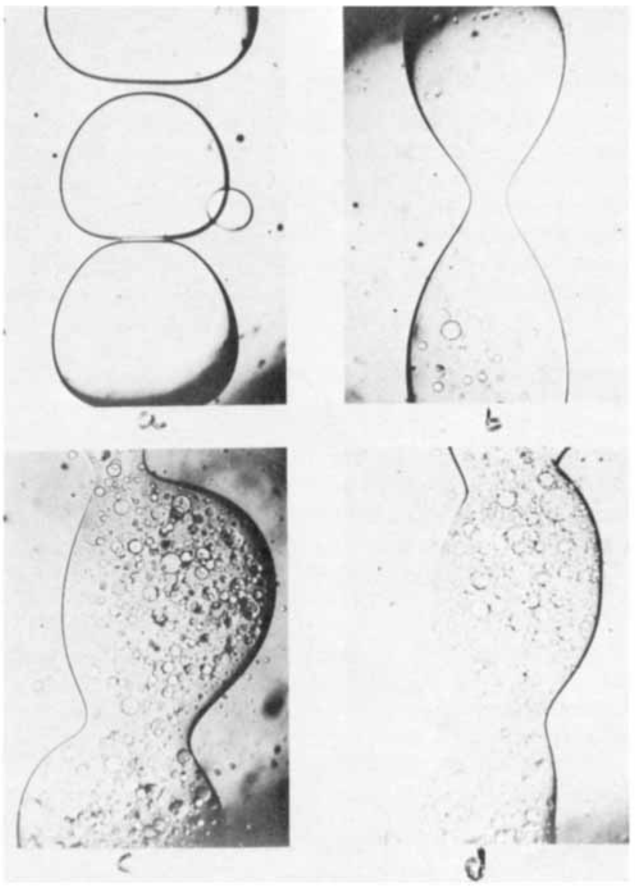


Fig. 12. Carbon tetrachloride into glycerine, No. 19 hypodermic needle, 5½ cm. from orifice. *a.* $N_{Re} = 7.4$. *b.* $N_{Re} = 35.9$. *c.* $N_{Re} = 48.6$. *d.* $N_{Re} = 63.4$.

The parameters of most immediate commercial interest are, of course, the percent included area and volume, here defined as

$$\%\ \text{included area} = \frac{\text{total surface area of inclusions} \times 100}{\text{total external surface of large drops}}$$

$$\%\ \text{included volume} = \frac{\text{total volume of inclusions} \times 100}{\text{total volume enclosed by external surface of large drops}}$$

Definition was made in this manner so ready estimates of corrections to existing data could be made.

An extremely naive model, but one which permits a reasonable correlation of the data, is a linear model for the relationship of the logarithms:

$$\log\ (\%\ \text{included volume}) = m_1 \log\ [(N_{Re})(N_{We})] + b_1$$

$$\log\ (\%\ \text{included area}) = m_2 \log\ [(N_{Re})(N_{We})] + b_2$$

A least-squares fit was run on these models, and the results are shown in Figures 10 and 11. These are the best fitting straight lines by using maximum likelihood estimation. The 95% confidence limit for the lines are shown for each case. A check on experimental error was made in the experimental work. Observed unexplained variation was of comparable magnitude with experimental error. This model indicates that inertial forces play the dominant role in inclusion formation. Without knowledge of the mechanism discussed below, it is somewhat surprising that a model based on nozzle parameters alone gives a reasonable correlation; however, when we consider this mechanism, it is not surprising that such an approach yields a good first approximation.

DETERMINATION OF MECHANISM

In low viscosity systems, breakup of the liquid jet occurs over such a short distance that it is not possible to resolve the breakup photographically. Accordingly, runs were made by using a low viscosity sprayed phase (carbon tetrachloride) and a highly viscous receiving fluid (glycerine).

Shown in Figure 12 (*a* through *d*) is a series of pictures taken with this liquid pair at progressively increasing nozzle velocities. As shown in the photographs, the high viscosity of the glycerine kept breakup of the jet in the varicose regime. A most embarrassing point in the analysis of the data to this time had been the question of how the inclusions could penetrate the relatively stable large drop configuration to get inside. The answer yielded by this set of photographs was that the inclusions were present in the jet before it disintegrated; the inclusions literally predate the large drops.

Next, pictures were taken closer to the nozzle in an attempt to catch the inclusions forming. Results are shown in Figures 13 (*a* through *c*). A ligament or sheet is drawn out from the jet, but, instead of breaking off, it recoalesces with the jet, pinching off some of the external phase in the process. This elongated form then collapses to form a drop or drops within the jet.

This mechanism was also confirmed by using high-speed cinematography. The films clearly showed the inclusions moving longitudinally within the jet prior to breakup, although sufficient combination of magnification and field could not be obtained to follow the recoalescence of ligaments with the jet.

Coalescence of the inclusions proceeds at a rapid rate, and the primary sink for inclusions is the wall of the jet or drop rather than coalescence of one inclusion with another. The rapid coalescence probably explains why multiple emulsion structures are so seldom detected except in highly viscous systems; by the time the system is observed, the inclusions have disappeared. A logical conclusion would seem to be that multiple emulsion structures are probably formed in almost all liquid-liquid processes but disappear before they are observed. For any sort of macroscopic approach, inclusion surface area would merely be lumped in the mass transfer coefficient, and inclusions would give observed effects which would be regarded as anomalies in the transfer coefficient rather than the interfacial area.

CONCLUSIONS

Both the mechanism proposed and the data taken indicate that multiple emulsion formation probably exists in many liquid-liquid problems but is seldom observed because of coalescence speed. Application of the log normal probability function to both the large drop and inclusion distribution gives reasonable answers. The proposed model for percent included area and volume will probably furnish order-of-magnitude results for a given liquid pair; however, caution should be used in extrapolating. Inertial forces predominate in the inclusion formation process, and in future work it will probably be necessary to consider all five variables in the Reynolds and Weber numbers.

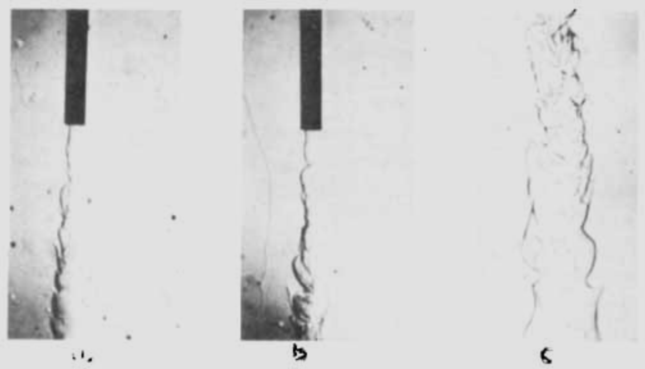


Fig. 13. Carbon tetrachloride into glycerine. *a*, *b*. No. 22 hypodermic needle. c. No. 19 hypodermic needle. 2.5 cm. from orifice. *a*. N_{Re} = 30.6. *b*. N_{Re} = 42.0. c. N_{Re} = 47.5.

NOTATION

D = large drop diameter, nozzle diameter
d = inclusion diameter
$f(z)$ = probability density function
$F(z)$ = probability distribution function (cumulative)
l_i = distance of travel of large drop of diameter D_i
M = maximum number of large drop diameter size classes
N, n = maximum number of inclusion diameter size classes, number of drops, parameter in probability density function
N_{Re} = Reynolds number = $D_n v_n \rho_s / \mu_s$
N_{We} = Weber number = $D_n v_n^2 \rho_s / \gamma$
O/W = oil-in-water emulsion
$Pr(\alpha)$ = probability of the event α
v_n = velocity through nozzle
V = volume of drops
W/O = water-in-oil emulsion
x_{ij} = number of inclusions of diameter d_j in large drops of diameter D_i
y_i = number of large drops of diameter D_i

Greek Letters

α, β = parameters in probability density function
γ = interfacial tension, parameter in probability density function
μ = viscosity
ρ = density
σ = standard deviation
$\omega = \dfrac{\log z - \log \overline{Z}_g}{\log \sigma_g}$

Superscripts

bar = mean
$\wedge$ = estimate from sample

Subscripts

g = geometric
n = nozzle
r = receiving phase
s = sprayed phase

LITERATURE CITED

1. Boll, R. H., Ph.D. dissertation. Univ. Mich, Ann Arbor (1955).
2. Clayton, W., "The Theory of Emulsions and Their Technical Treatment," 5 ed., Churchill, London, England (1954).
3. Pavloshenko, I. S., and A. V. Yanishevskii, *Zh. Prikl. Khim.*, 32, 1495-1502 (1959).
4. Putnam, A. A., et al., *WADC Tech. Rept. 56-344* (Mar., 1957).
5. York, J. L., Ph.D. dissertation, Univ. Mich. Ann Arbor (1949).

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