Prediction of Drop Volumes in Liquid–Liquid Systems

A method is described for calculating drop sizes obtained in Newtonian immiscible liquid-liquid systems when a dispersed fluid is continuously injected at uniform subjetting point velocities through a sharp-edged nozzle that is preferentially wet by the continuous phase. This method is based on the calculation of the shape of a drop forming at the nozzle tip by means of a pressure balance over the drop interface and the use of a force balance to determine if any portion of the forming drop can break away. Calculated drop sizes are compared with experimental data for systems of different physical properties.

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SCOPE

The importance of drop size and interfacial area in liquid-liquid systems has prompted many investigations to obtain a reliable correlation for predicting the size of drops produced when dispersing one liquid into a second immiscible liquid through orifices and nozzles. These investigations have resulted in correlations which approximate experimental results with varying degrees of success but which suffer from the limitation of empiricism inherent in their development.

The present work has produced a method for predicting the size of drops in Newtonian liquid-liquid systems where the dispersed phase is continuously injected at uniform subjetting velocities through a nozzle into a continuous phase that preferentially wets the nozzle tip. This method does not suffer from the degree of empiricism that other correlations do because it does not rely on dimensional analysis or on the Harkins coefficient for its development. In each system studied, the present method predicts drop sizes that agree more closely with experimental results than do all the other correlations tested.

CONCLUSIONS AND SIGNIFICANCE

A method is described that predicts the size of drops produced in immiscible liquid-liquid systems when the dispersed phase is injected at uniform subjetting velocities through a cylindrical nozzle into a stationary continuous phase that preferentially wets the nozzle tip. This method differs from other correlations in that the shapes of drops forming at the nozzle are calculated from the properties of the system by means of a pressure balance made across the drop interface. Force balances of the buoyancy, momentum, viscous drag, and interfacial tension are then made at horizontal sections throughout the drop. If, at some horizontal section the net upward forces are positive, the growing drop is assumed to pinch off and break away at the section. The predicted drop size is the smallest calculated drop that will break away.

There is close agreement between the predicted drop volume curves and experimental values for systems varying widely in physical properties of interfacial tension, viscosity, and density.

The significance of this work is that as a result of its lesser degree of empiricism, this method should have greater reliability over wider ranges of system properties than that of previous correlations.

Many investigations have been made to obtain reliable relationships for calculating the volumes of drops produced when dispersing one liquid through a nozzle into another. They have produced empirical or semi-empirical correlations that approximate experimental results with varying degrees of precision. These reported correlations are well discussed by Scheele and Meister (1968), and Heertjes, de Nie, and de Vries (1971).

This paper describes a method of calculation based not upon the usual model of a forming drop made up of simple geometric shapes but upon a calculated shape obtained from a pressure balance taken across the interface between the inside and outside of the drop forming at a nozzle tip. A vertical force balance is then made throughout the forming drop to determine where the drop pinches off and breaks away from the nozzle. This method does not suffer from the limits of empiricism of equations developed by dimensional analysis.

Bashforth and Adams (1883) obtained a relationship for the profile of a static drop sitting on a plate not wetted by the drop, and also for a pendent drop, by taking a pressure balance over the drop interface and assuming that the drop was symmetrical about its vertical axis. In order to obtain the profile of a drop forming on an orifice plate, Halligan and Burkhart (1968), extended this work by adding a momentum term that assumed the flow through the orifice into the forming drop impinged on the underside of the interface at the top of the drop surface before being deflected around the drop interface. This model results in an abnormally high predicted pressure at the area of impingement when compared to that over the rest of the surface. This present investigation assumes that the entering dispersed phase circulates within the drop forming at the nozzle, and thereby increases the outward pressure on the interface evenly throughout.

Photographic studies have shown that drops forming at a nozzle tip are symmetrical about the center line axis if no surface active agents are present at the nozzle tip. Consequently, from the meridian profile shape, the surface area and the volume of the forming drop can be readily

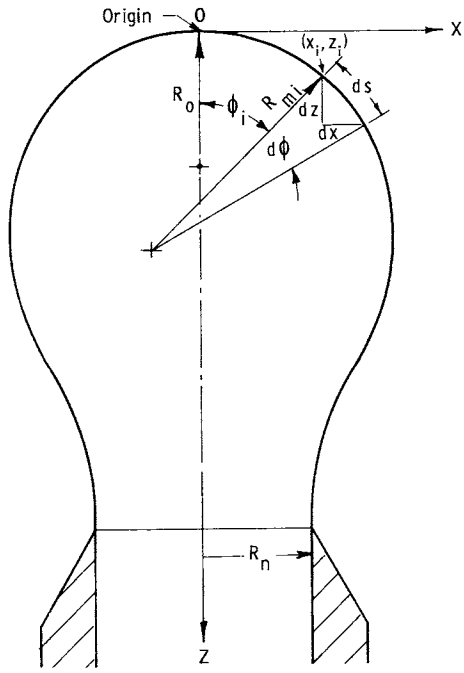

Fig. 1. Coordinate system.

calculated between the top of the drop and any horizontal plane passing through the drop.

THEORY

Calculation of a Forming Drop Profile

For calculating coordinates of points on the drop profile, the origin is taken at the intersection between vertical centerline axis and interface at the top of the drop. The x axis is taken to be horizontal and the z axis vertical, the positive direction being downward (Figure 1). x and z are the coordinates of a point on the meridian profile, R_m is the radius of curvature of the meridian section at that point, and ϕ is the angle that the normal to that section makes with the centerline axis. Using the work of Bashforth and Adams (1883), a pressure balance taken over the drop interface results in

$$\frac{1}{R_m} + \frac{\text{Sin}\,\phi}{x} = \frac{2}{R_o} + \frac{g(\rho_D - \rho_C)z}{\sigma} \qquad (1)$$

where R_o is the meridian radius of the drop at the origin, $\rho_D - \rho_C$ is the difference in density between the fluid inside and outside of the drop, and σ is the interfacial tension.

Linear dimensions that are made dimensionless are indicated by superscript *. Making Equation (1) dimensionless by multiplying by R_o produces

$$\frac{1}{R_m^*} = 2.0 + \beta z^* - \frac{\text{Sin}\,\phi}{x^*} \qquad (2)$$

where

$$\beta = \frac{g(\rho_D - \rho_C)R_o^2}{\sigma} \quad \text{(dimensionless)} \qquad (3)$$

By taking small incremental lengths ds along the profile of the drop, Bashforth and Adams (1883) and Halligan and Burkhart (1968a) obtained the following differential equations and associated boundary conditions

At increment i / At origin

$$\frac{dx^*}{ds^*} = \text{Cos}\,\phi \qquad \left(\frac{dx^*}{ds^*}\right)_0 = 1.0 \qquad (4)$$

$$\frac{dz^*}{ds^*} = \text{Sin}\,\phi \qquad \left(\frac{dz^*}{ds^*}\right)_0 = 0 \qquad (5)$$

$$\frac{d\phi}{ds^*} = \frac{1}{R_m^*} \qquad \left(\frac{d\phi}{ds^*}\right)_0 = 1.0 \qquad (6)$$

In the present work, coordinates of points on the meridian drop profile are calculated by integrating Equations (4), (5), and (6) commencing at the origin where $x^* = 0$, $z^* = 0$, and $R_m^* = 1$. For each increment, values for ϕ, x^*, and z^* are then computed from Equations (4), (5), and (6), which in turn are used in Equation (2) for the calculation of R_m^*. The numerical integration is carried out until $x = R_n$ with x decreasing and $d\phi$ positive (outside of drop convex) as shown in Figure 2a, or with x increasing and $d\phi$ negative (outside of drop concave) as shown in Figure 2c.

As the value of R_o is unknown, a value is assumed. The drop profile is then calculated, after which a force balance is taken to determine whether or not the upward forces exceed the downward forces at any horizontal section throughout the drop. If the upward forces do not exceed the downward forces, the value of R_o is increased and the process repeated. In most cases, before the upward forces exceed the downward, a critical value of R_o is obtained, above which the drop profile shape changes from that as shown in Figure 2a to that as shown in Figure 2b. Since x is increasing and greater than R_n, and $d\phi$ is negative, the profile fails to meet the nozzle tip. Equation (2) does not take into account the constraint between the adhesive forces of the nozzle and the drop interface. Where the adhesive forces are significant, a drop profile similar to that shown in Figure 2c results. It is assumed that the effect of this drawing-in at the bottom of the drop as shown in Figure 2c is to produce an additional inward pressure on the interface varying linearly from a maximum at the bottom to zero at the top of the drop. Thus, to allow for this an additional dimensionless factor γ is added to Equation (2) to produce

$$\frac{1}{R_m^*} = 2.0 + \beta z^* - \frac{\text{Sin}\,\phi}{x^*} + \gamma z^* \qquad (7)$$

where γ is the effect of the forces of adhesion between the interface and the nozzle tip. This is the same equation as that obtained by Halligan and Burkhart (1968b) and by Halligan and Agrawal (1971).

If for selected values R_o and γ, the calculated drop profile fails to touch the nozzle tip (Figure 2b), γ is increased and the process repeated until the drop profile just touches the nozzle tip (Figure 2c). If then the upward forces exceed the downward at a horizontal section of the forming drop, the drop will pinch off and break away at that sec-

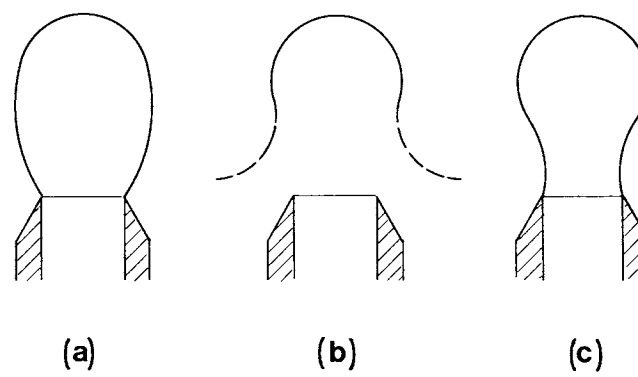

Fig. 2. Typical calculated drop profiles.

tion. If, however, at no horizontal section do the upward forces exceed the downward, the drop will remain at the nozzle.

For each value of R_o, values of γ are iterated until the profile of the drop just touches the nozzle tip, that is, moves from Figure 2b to 2c. Values of R_o are iterated until the minimum value of R_o is obtained for the drop to pinch off and break away.

By integrating the profile as a volume of revolution and as a surface of revolution about the vertical axis of symmetry between the origin and a horizontal section of the drop, the volume and the surface area of the forming drop above that section are obtained.

FORCE BALANCE

The forces acting upward on the drop during formation at the horizontal section at some increment i of the integration are

1. Buoyancy of forming drop above horizontal plane i

$$F_B = V_i g\,(\rho_C - \rho_D) \tag{8}$$

where V_i is a volume of the forming drop above plane i

2. Momentum force due to change of momentum in the forming drop. The momentum loss in the drop is assumed to be equal to the momentum gained by the mass of continuous phase which moves with the drop. The total travelling mass when a sphere submerged in the continuous phase is moving perpendicularly away from a wall is shown by Milne and Thompson (1962) to be

$$M_T = \frac{1}{2}\left(2M + M^1 + \frac{3}{8}M^1\frac{a^3}{h^3}\right) \tag{9}$$

where M is the mass of the sphere, M^1 the mass of the continuous phase displaced by the sphere, a the radius of the sphere, and h the distance from the center of the sphere to the wall. By approximating the drop forming at the nozzle as a sphere, and since

$$h^3 >> a^3,$$

$$M_T = \frac{2M + M^1}{2} \tag{10}$$

The ratio of the drop mass to the travelling mass is

$$\frac{2M}{2M + M^1} = \frac{2\rho_D}{2\rho_D + \rho_C} \tag{11}$$

Since the input momentum from laminar flow through the nozzle is

$$\frac{4}{3}\,\frac{m^2}{\rho_D\,\pi\,R_n^2} \tag{12}$$

the momentum force on drop is

$$F_M = \frac{4m^2}{3\rho_D\,\pi\,R_n^2}\left(1 - \frac{2\rho_D}{2\rho_D + \rho_C}\right) \tag{13}$$

The forces acting downward on the drop during formation at horizontal section increment i are

1. Interfacial tension force

$$F_T = 2\pi x_i \sigma\ \mathrm{Sin}\ \phi_i \tag{14}$$

2. Viscous drag force where circulation is present in drops moving in continuous phase. Batchelor (1967) gives the following relations for the calculation of drag force

$$F_D = 4\pi a \mu_C U\left(\frac{\mu_C + 1.5\,\mu_D}{\mu_C + \mu_D}\right) \tag{15}$$

For calculating the drag force on the forming drop, the velocity of the uppermost surface of the drop is approximated by assuming the drop to be a growing sphere of radius equal to the maximum x coordinate x_{max} of the calculated drop profile and to be sitting on the nozzle tip. Consequently the upward velocity of the uppermost surface is twice the rate of change of the radius of the growing sphere. For estimating this upward velocity

$$\frac{dV}{dt} = 4\pi x^2_{max} \cdot \frac{dx}{dt} \tag{16}$$

$$= \frac{m}{\rho_D} \cdot \tag{17}$$

The upward velocity at the top of the drop

$$U = 2\,\frac{dx}{dt} \tag{18}$$

Therefore,

$$U = \frac{m}{2\pi x^2_{max}\rho_D} \tag{19}$$

By substituting x_{max} for a and Equation (19) into Equation (15) the expression for drag force becomes

$$F_D = \frac{2m\mu_C}{\rho_D x_{max}}\left(\frac{\mu_C + 1.5\,\mu_D}{\mu_C + \mu_D}\right) \tag{20}$$

Adding the vertical forces acting on the drop during formation at a horizontal section increment i produces the net upward force

$$F_{net} = F_B + F_M - F_T - F_D \tag{21}$$

$$= V_i g(\rho_C - \rho_D) + \frac{4}{3}\left(1 - \frac{2\rho_D}{2\rho_D + \rho_C}\right)\left(\frac{m^2}{\rho_D \pi R_n^2}\right)$$

$$- 2\pi x_i \sigma\ \mathrm{Sin}\ \phi_i - \frac{2m\mu_C}{\rho_D x_{max}}\left(\frac{\mu_C + 1.5\mu_D}{\mu_C + \mu_D}\right) \tag{22}$$

For a drop to pinch off and break away at some horizontal section, the net upward force F_{net} must be greater than zero at that section. The volume of the drop pinching off and breaking away is assumed equal to that of the forming drop above that section at the instant of the commencement of breakaway.

Typical values for the force terms in Equation (21) are given in Table 1 for the systems shown in Figures 3 and 5. When the continuous phase viscosity is less than 0.01 poise, the drag force is very small. At low nozzle velocities both the momentum and the drag forces are small.

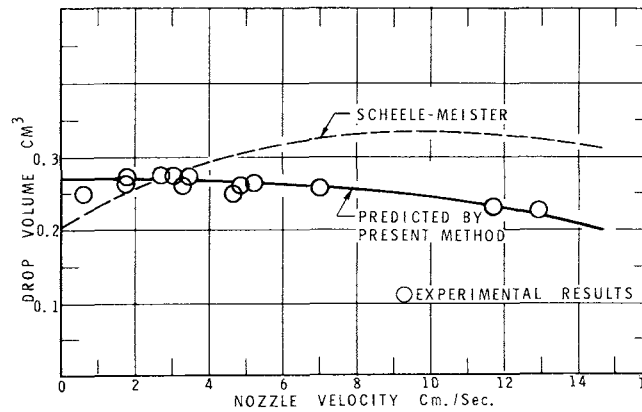

Fig. 3. Drop volume nozzle velocity dependence for benzene dispersed into water. Nozzle diameter = 0.325 cm.

TABLE 1. TYPICAL VALUES FOR TERMS IN EQUATION (21)

System	Nozzle velocity cm/s	Viscosity poise μ_c	Force terms dynes F_B	F_M	F_T	F_D
Benzene-water	13.75	0.01	25.5	6.6	32.0	0.1
Heptane-glycerine	28.17	5.15	14.1	1.8	7.2	8.7

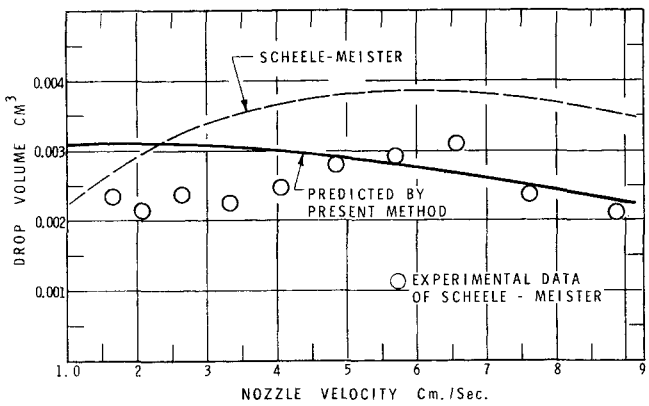

Fig. 4. Drop volume nozzle velocity dependence for butyl alcohol dispersed into water. Nozzle diameter = 0.0813 cm.

EXPERIMENT

Experimental studies were made to determine the volume of drops produced when dispersing benzene through a cylindrical sharp edged brass nozzle at different uniform velocities into a stationary water continuous phase, each phase being mutually saturated. Nozzles with inside diameters of 0.280, 0.325, 0.410 cm were used. Drop volumes were obtained from the measurements of the number of drops per second produced at different measured uniform rates of flow through the nozzle under study. The number of drops per second was measured by direct observation with a stop watch for low rates by means of a Strobtac for medium rates and by cine photography for higher rates. The Strobtac could be used only where the rate of drop formation was sufficiently uniform to permit the rising drops to appear stationary when synchronized with the Strob light. At input velocities higher than 10 cm/s through the nozzle but below the jetting point, the nonuniformity of the drops produced increased with the increase of velocity. Flow rates were measured by means of a graduated cylinder and a stop watch.

Great care was taken to eliminate impurities from the system, as even small traces of surface active materials were found to create significant abnormalities in previous work on discontinuous injection by Izard, Cavers, and Forsyth (1963). In the apparatus used, the phases contacted only glass, copper, and Teflon. The precision of measurement was approximately 5% at input rates of less than 10 cm/s through the nozzles under study.

All measurements were made at 70° ± 0.5°F. Interfacial tension between benzene and water was measured by means of a Dunuoy Tensiometer to be 31.36 dynes/cm. Densities of the mutually saturated phases were by means of free floats, the density of the continuous water phase being 0.9975 g/cc and that of the benzene dispersed phase 0.877 g/cc.

DISCUSSION OF RESULTS

Comparisons between experimental data, the predicted drop volumes from the present method, and the calculated drop volumes from the correlation of Scheele and Meister (1968), are illustrated in Figures 3 to 6. This correlation has been selected for purposes of comparison as it agrees more closely with the experimental results than do the correlations of other previous investigations.

Figure 3 demonstrates very close agreement between the predicted values by the present method and the experimental values of drop volumes when dispersing benzene through a sharp edged brass nozzle of 0.325 cm I.D. into a continuous stationary water phase, both phases being mutually saturated and with no solute mass transfer taking place. Results with 0.280 and 0.410 cm I.D. nozzles produced similarly good agreement between the predicted and experimental values.

Figures 4, 5, and 6 illustrate the good agreement between the predicted values of drop volumes from the present work and the experimental data of Scheele and Meister (1968), supplied by Scheele (1971), for the butanol-water system (low interfacial tension), the heptane-glycerine system (high continuous phase viscosity: 515 centipoise), and the three component system with a carbon tetrachloride and heptane solution dispersed phase-water phase system (very small density difference between the phases). The predicted curve for the butanol-water system agrees more closely with the experimental data than does the calculated curve from the correlation of Scheele and Meister (1968). A similar finding with the heptane-glycerine system (high continuous phase viscosity), confirms the validity of Equation (20).

Figure 6 shows comparison between the calculated prediction curve of Scheele and Meister (1968) and their experimental data obtained from dispersing carbon tetrachloride heptane solution into water in such proportions that the density difference between the continuous and the

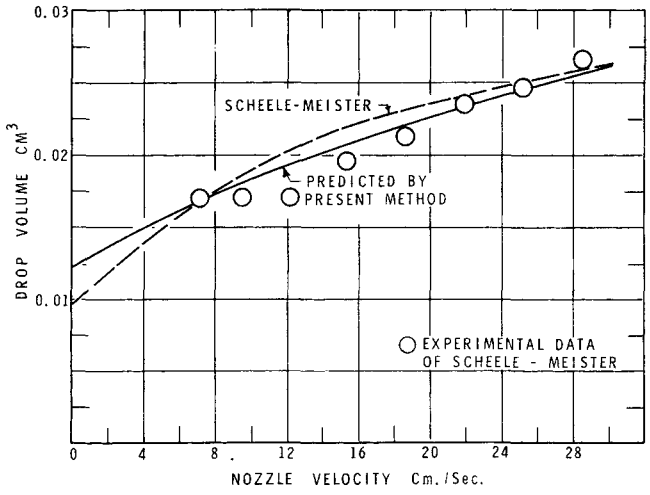

Fig. 5. Drop volume nozzle velocity dependence for *n*-heptane dispersed in glycerine. Nozzle diameter = 0.0813 cm.

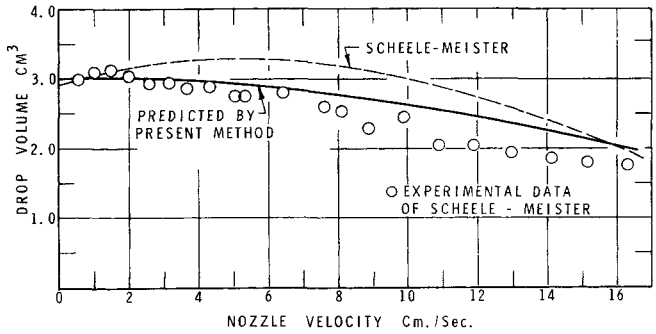

Fig. 6. Drop volume nozzle velocity dependence for 55% carbon tetrachloride and 45% heptane dispersed into water. Nozzle diameter = 0.254 cm.

dispersed phases was very small. Their plotted prediction curve is based on measured values of 0.996 g/cc for the density of water and of 0.988 g/cc for the density of the dispersed phase as supplied by Scheele (1971). Since these reported density values produced computed drop volumes by the present method that were considerably larger than the experimental volumes, a density value of 0.998 g/cc was used for the continuous phase (the accepted value at 20°C) and 0.986 g/cc for the density for the dispersed phase for calculation of the predicted curve by the present method. These values in each case differ by 0.002 g/cc from the values reported by Scheele (1971). Weissberger (1960) states that the accuracy of density measurements made with free floats is not better than ± 0.001 g/cc. Also, in order to approach this degree of accuracy each liquid requires a different float calibration because of differences in surface tension and in wetting. The deviation of 0.002 g/cc in the values used from the experimentally obtained values is considered to be within the boundaries of experimental accuracy. Also, a free float calibrated in water and used to measure the density of a liquid of less than half the surface tension would in all probability give an abnormally high value for the density reading of that liquid. By using these revised values that lie within the boundaries of experimental accuracy of the measured densities for the system, as shown in Figure 6, close agreement is obtained between the experimental values and the curve predicted by the theory of the present paper.

CONCLUSION

The present method of predicting the volume of drops produced when dispersing a liquid through a sharp edged cylindrical nozzle at uniform subjetting velocities into a stationary continuous phase that preferentially wets the nozzle tip and under conditions of no mass transfer, has produced a correlation that more closely fits the experimental data of the systems examined than do those reported by other investigators. This improved correlation has resulted from the reduction of empiricism and by limiting the use of spherical models to the determination of only the momentum and drag force terms. The close agreement at higher input nozzle velocities between the predicted and the experimental values for drop volumes for the systems studied, confirms the validity of the momentum force term. The close agreement for the heptane-glycerine system (high continuous phase viscosity) confirms the validity of the drag force term.

The present method has the added advantage that the volume and the surface area of the forming drop, as well as that of the drop breaking away, can be obtained readily.

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NOTATION

a = sphere radius, cm
F_B = buoyancy force, dynes
F_D = viscous drag force, dynes
F_M = momentum force, dynes
F_{net} = net upward force, dynes
F_T = interfacial tension force, dynes
g = acceleration of gravity, 980.8 cm/s^2
m = mass input of dispersed phase through nozzle, g/s
M = mass of drop, g
M^1 = mass of continuous phase displaced by drop, g
M_T = travelling mass of drop and adjacent continuous phase, g
R_m = meridian radius of drop at point (x, z) cm
R_m^* = dimensionless meridian radius, $R_m^* = R_m/R_o$
R_n = radius of nozzle, cm
R_o = meridian radius of drop at origin, cm
ds = incremental length of drop profile, cm
ds^* = dimensionless incremental length of drop profile, $ds^* = ds/R_o$
U = velocity of leading surface of forming drop, cm/s
V = volume of sphere, cc
V_i = volume of forming drop above horizontal section at increment i, cc
x = x coordinate, cm
x^* = dimensionless x coordinate, $x^* = x/R_o$
z = z coordinate, cm
z^* = dimensionless z coordinate, $z^* = z/R_o$
β = dimensionless group defined by Equation (3)
γ = dimensionless term—constraint between nozzle tip and drop interface
μ_C = viscosity of continuous phase, g/cm s
μ_D = viscosity of dispersed phase, g/cm s
π = 3.14159
ρ_C = density of continuous phase, g/cc
ρ_D = density of dispersed phase, g/cc
σ = interfacial tension between dispersed and continuous phase, dynes/cm
ϕ = angle between vertical axis and normal to meridian profile at point (x, z), radians

Subscripts and Superscripts

o = origin
i = increment number
max = maximum value
* = dimensionless

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