Formation of Organic Drops in Water

L. E. M. de CHAZAL and J. T. RYAN
University of Missouri, Columbia, Missouri

Drop formation from submerged nozzles was studied using liquid-liquid systems of widely varying properties. The data were correlated using a momentum balance and a two-stage process of drop formation. The average agreement between data and correlation was 6.3%.

The first attempt to explain quantitatively the phenomenon of static drop formation from circular nozzles was made by Tate (*12*). This work was later expanded by Adams and Bashforth (*1*) and by Harkins (*4*). Harkins' experimental results and correlation are now accepted as standard in the field. Efforts at more rigorous mathematical treatment have been made (*1*, *9*), but have not succeeded in displacing the Harkins treatment.

The study of drop formation under dynamic conditions came at a much later date. Hayworth and Treybal (*5*), Batson (*2*), Null and Johnson (*7*), and Christiansen and Hixon (*3*), who all published in the last decade, were among the important early contributors to the field. Data and theory continue to be presented, with Rao et al. (*8*) and Scheele and Meister (*11*) as examples of important recent contributors.

Unlike the case under static conditions, the problem of obtaining good data under conditions of flow is serious. Drop volume is much harder to measure, and important factors such as surface tension may change during the period of drop formation due to the migration of surface-active impurities. Consequently, stringent measures were taken to prevent the accidental insertion of impurities, and positive displacement techniques were used to determine the volume of the drops.

EXPERIMENTAL PROCEDURE

In the experiments reported here, five organic liquids were dispersed into distilled water from circular nozzles. Water-saturated hexane, benzene, methyl isobutyl ketone, phenetole, and cyclohexanol were used as dispersed phases. The physical properties of these immiscible pairs are given in Table 1.

Interfacial tension changes drastically with the presence of small concentrations of contaminants. Hence particular attention was paid to the purity of the materials and to equipment cleanliness. All organic liquids (technical grade or better) were batch distilled, the first and last 20% of each batch discarded. Glassware used in the preparation and storage of the liquids was cleaned in a hot chromic acid solution and then thoroughly rinsed with distilled water. To prevent contamination of the liquids by parts of apparatus, only stainless steel, virgin Teflon, and glass were used in its construction. As a further precaution, the apparatus was completely dismantled and cleaned with a hot acid solution between runs.

The experimental apparatus (see Figure 1) consisted of a set of positive displacement piston pumps, a chamber, and drop detection and counting circuits. The pumping system included two pairs of piston pumps, used for separate flow ranges; these were driven through a variable speed transmission by a syncronous motor. While one of the pumps was metering liquid to the chamber, the other in the pair was being filled.

The drop-formation chamber was constructed of a 3-ft. section of 12-in. stainless steel pipe. Six glass view ports were provided for the observation of the drops during formation and after detachment. The chamber was sealed at both ends by removable lids. Thus the whole system was closed to the atmosphere, and accidental pollution by dust, etc., was avoided.

Four nozzles, with internal radii of 0.203, 0.167, 0.147, and 0.113 cm., respectively, were used in this study. The nozzles were constructed from high-pressure stainless steel tubing. The tubing was first drilled to the approximate diameter and then reamed to the diameters indicated above. The ends of the nozzles were beveled to 45 deg. and polished.

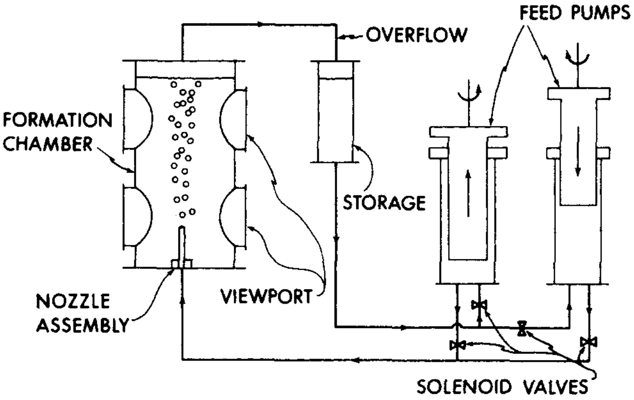

Fig. 1. Experimental apparatus.

At high pumping rates, drop frequency was measured with a photodiode and a scalar. A collimated light beam was passed above the nozzle and onto the photodiode. The forming drop interrupted the light beam and decreased the light intensity of the photodiode. The resulting voltage change was digitized and registered by the scalar. The number of drops formed was counted in this manner for a fixed period of 30 sec. or 1 min. The rotational speed of the pump shaft, and consequently the pumping rate, was measured by a similar technique. Details of the circuit designs can be found elsewhere (*10*). At low rates both drop frequency and pumping rate were timed with a stopwatch.

The procedure followed for each system was identical. The apparatus was dismantled, cleaned, and reassembled. The previously purified pair of liquids was introduced into the chamber and violently agitated by blowing filtered air through the nozzle for 24 hr. Additional water was then added to the chamber, and the organic liquid circulated through the system for another 24 hr. As shown by tests of interfacial tension, the two phases were then mutually saturated. The pumps were turned on and any air present was bled from the system. The transmission speed was adjusted to give a drop frequency of approximately 1/sec., and the data recorded. Advancement of the transmission speed continued until multiple drops were formed at the end of a jet. The next nozzle to be used was inserted and the procedure was repeated.

TABLE 1. PHYSICAL PROPERTIES OF LIQUIDS USED

	Viscosity, centipoise	Density, g./cc.	σ, dynes/cm.	Temp., °F.
Hexane	0.294	0.6552	49.5	71 ± 0.5
Water	0.887	0.9957		
Benzene	0.598	0.8722	34.1	71 ± 0.5
Water	0.478	0.9947		
Methyl isobutyl ketone	0.478	0.7980	9.7	71 ± 0.5
Water	0.894	0.9948		
Cyclohexanol	17.25	0.9496	3.9	71 ± 0.5
Water	1.024	0.9952		
Phenetole	0.956	0.9581	29.1	76 ± 0.5
Water	0.942	0.9954		

J. T. Ryan is at the University of Alberta, Edmonton, Canada.

THEORY

An analysis of the drop-formation process should involve the solution of the Navier-Stokes equation along with the proper boundary conditions. However, the mathematical complexities of the equation, considering the existence of a free boundary, precludes this approach to the problem. As an alternative, an overall momentum balance on the forming drop is used here.

The time required for a drop to form can be divided into two parts. First, the time required for the drop to reach its unstable or "necking-in" state; and second, the time for the drop to detach completely after instability has occurred.

The first stage of the formation process may be analyzed by applying Newton's second law of motion to the drop at the instant of instability. The forces considered to be acting on the drop are the buoyancy, the interfacial tension at the nozzle, and the momentum of the entering fluid. Drag on the forming drop is neglected. However, the effect of the continuous phase viscosity is taken into account during the second stage of formation.

The simplified equation describing the momentum change of the forming drop is

$$\frac{d(MU)}{dt} = \Delta\rho g V_1 + \rho_D Q \frac{(U^2)_{\mathrm{Ave}}}{U_{\mathrm{Ave}}} - 2\pi R_N \sigma \Psi \tag{1}$$

where the three terms on the right represent buoyancy, momentum flux, and the restraining force due to interfacial tension at the nozzle. Ψ is the Harkins correction factor (*4*).

Null and Johnson (*7*) have obtained data which show that the velocity of the leading edge of the drop is constant prior to the necking-in process. Assuming that velocity of the drop is proportional to the nozzle velocity and performing the differentiation, one can rewrite Equation (1) as

$$\Delta\rho g V_1 = 2\pi R_N \sigma \psi - C_1 \rho_D Q \frac{(U^2)_{\mathrm{Ave}}}{U_{\mathrm{Ave}}} \tag{2}$$

where C_1 is a coefficient to be determined experimentally. Equation (2) must be applied at the point at which the drop necks in for detachment, since this is where the forces on the drop are balanced.

Unless a jet is formed, the neck has the same diameter as the nozzle, and the momentum term in Equation (2) can be evaluated in the form

$$\rho_D Q \frac{(U^2)_{\mathrm{Ave}}}{U_{\mathrm{Ave}}} = \frac{4}{3} \frac{\rho_D Q_2^2}{\pi R_N^2} \tag{3}$$

When a jet is formed, the neck may be of much smaller diameter, and the momentum is correspondingly larger. Fortunately, the ratio of jet diameter to nozzle diameter is very nearly a linear function of the square root of the Bond number, $\Delta\rho g R_N^2/\sigma$. This has been shown to be the case at the point of largest diameter (*3*), and is approximated for the point of least diameter by

$$\frac{R_N}{R_j} = 1 + C_2 \sqrt{\frac{\Delta\rho g R_N^2}{\sigma}} \tag{4}$$

where the value of the constant C_2 is not directly evaluated because it is subsequently incorporated into other constants.

Using Equation (4) to determine the value of R_j in terms of R_N, the momentum term in Equation (2) becomes, when a jet exists

$$\rho_D Q \frac{(U^2)_{\mathrm{Ave}}}{U_{\mathrm{Ave}}} = \frac{4\rho_D Q^2}{3\pi R_N^2} \left[1 + 2C_2 \sqrt{\frac{\Delta\rho g R_N^2}{\sigma}} + \frac{C_2^2 \Delta\rho g R_N^2}{\sigma}\right] \tag{5}$$

In the systems studied the Bond number was much less than unity, and the last term in the parenthesis could be neglected.

During the time interval between the start of the necking-in process and complete detachment, additional fluid enters the drop. Denoting the time interval during which this process occurs as t_2, and the incremental drop volume as V_2, one can write

$$V_2 = Q t_2 \tag{6}$$

The necking time t_2 should be proportional to neck diameter and inversely proportional to drop velocity. Since these two variables are related to the better known drop diameter D_D and the terminal velocity U_t of the drop, both measured after detachment, it is convenient to express t_2 as

$$t_2 = \frac{C_3 D_D}{U_t} \tag{7}$$

and V_2 becomes

$$V_2 = \frac{C_3 D_D Q}{U_t} \tag{8}$$

Multiplying Equation (8) by $\Delta\rho g$ and adding the result to Equation (2), one can write the expression for the total drop volume as

$$\Delta\rho g V_D = 2\pi R_N \sigma \psi + C_3 \frac{D_D Q}{U_t} - C_1 \rho_D Q \frac{(U^2)_{\mathrm{Ave}}}{U_{\mathrm{Ave}}} \tag{9}$$

where either Equation (3) or Equation (5) is used to evaluate the last term in Equation (9). This equation is readily seen to reduce to Harkins' drop weight formula when the velocity is zero.

The velocity U_t was calculated by the correlation of Hu and Kintner (*6*), and the values of the constants were calculated by regression analysis. In this process the values of ψ used where obtained from Harkins' correlation of $\psi VSR_D/V_D^{1/3}$, using the measured values of R_N and V_D. The final form, Equation (10), fit our 500 data points to an average error of 6.3%:

$$V_D = \frac{2\pi R_N \sigma}{g\Delta\rho}\left[\Psi + 1.648 \frac{g\Delta\rho R_N U_N V_D^{1/3}}{\sigma U_t} - 0.857 \frac{\rho_D R_N U_N^2}{\sigma}(1 + \beta)\right] \tag{10}$$

where

$\beta = 0$ in the nonjetting region (11*a*)

$\beta = 0.286 \sqrt{\Delta\rho g R_N^2/\sigma}$ in the jetting region (11*b*)

Ψ = Harkins' correction factor

Although it was not found possible to predict exactly when the formation of short jets occurred, all systems studied showed a marked increase in drop frequency at the time the jet elongated significantly. It is at this time that the quantity β in Equation (10) becomes significantly nonzero. This point was found to correspond to the following equality:

$$\sqrt{\frac{\rho_D R_N U_N^2}{\sigma}} = 1.07 - 0.75 \sqrt{\frac{\Delta\rho g R_N^2}{\sigma}} \tag{12}$$

Equation (12) was used to select the value of β in Equation (10). Whenever the left member was less than the right member, β was set to zero. When the left member was the greater, β was calculated by means of Equation (11*b*).

Equation (10) is valid only when single drops are formed. At high flow rates, where drop swarms are formed, the correlation has no validity. The upper limit of applicability is given by the following equality:

$$U_N = \frac{0.82\,\Delta\rho}{\rho_D}\,(gR_N)^{1/2}\left(\frac{\sigma}{g\Delta\rho R_N^2}\right)^{0.95} \qquad (13)$$

The form of Equation (13) was obtained by dimensional analysis, and the constants evaluated by curve fitting. It should be noted that accurate prediction of drop volume using Equation (10) requires that the value of ψ be obtained from Harkins' correlation. This is an iterative process, since V_D is unknown. However, the value $\psi = 0.625$ is correct to within 5% over the range of most practical applications, and may thus be used with good results.

RESULTS AND DISCUSSION

Results for four of the systems studied are presented as plots of drop volume versus flow rate in Figures 2 to 5. In all four plots the curve representing Equation (10) is drawn for the data taken with the nozzles of radii of 0.113 and 0.203 cm., respectively. Curves representing the correlation of Scheele and Meister (*11*), which appears to be the best published to date, are drawn for comparison.

The fit between Equation (10) and the data is on the average within 6.3%. The data for the system cyclohexanol-water are not presented because they are suspect. Deviations between data and Equation (10) amounted to as much as 20% in that system. Subsequent tests have shown that temperature fluctuations of 1°C., such as occurred during the runs, could account for the deviations observed. The influence of temperature on interfacial tension and on dispersed phase viscosity was particularly high for cyclohexanol, and the calculations were performed with the properties at the time-averaged temperature.

Comparison of the correlation of Scheele and Meister with Equation (10) shows that, while the shapes of the two curves are roughly comparable, the Scheele correlation falls more than 50% high at the upper limit for three of the four systems. The difference lies in the data to which the equations were fitted. In principle, the method of measurement of drop size and flow rates used in this study is independent of flow rate. In practice, because measurements were made for fixed time intervals, the precision increased slightly with increased flow rate. On the other hand, the opposite may be true of the Scheele and Meister technique. This is in part due to the increased difficulty of accurate drop volume measurement beyond the point where they distort. Perhaps more important, the presence of Calco Red Oil in the dispersed phase could cause unsuspected aberations. Plans to test this possibility are under way. Replicate runs, with and without the oil as solute, will be made in our equipment. Since the oil cannot influence our positive displacement technique, the effect on actual drop size and on the photographic technique can be assessed. The results of this test will be reported at a later date.

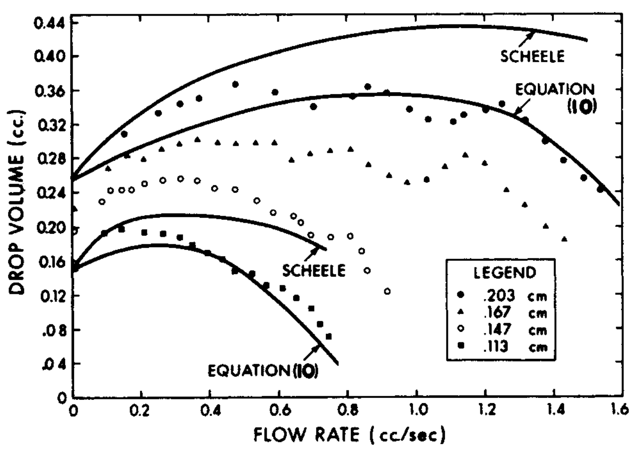

Fig. 2. Benzene-water system.

ACKNOWLEDGMENTS

This work was carried out under the sponsorship of the National Science Foundation. Thanks are also due to the Texaco Corporation, which provided a one-year graduate fellowship.

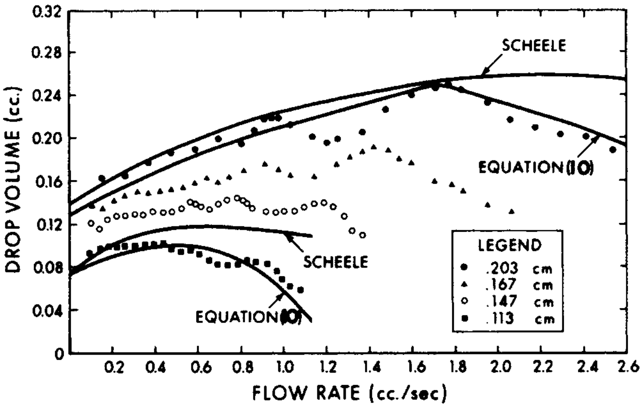

Fig. 3. Hexane-water system.

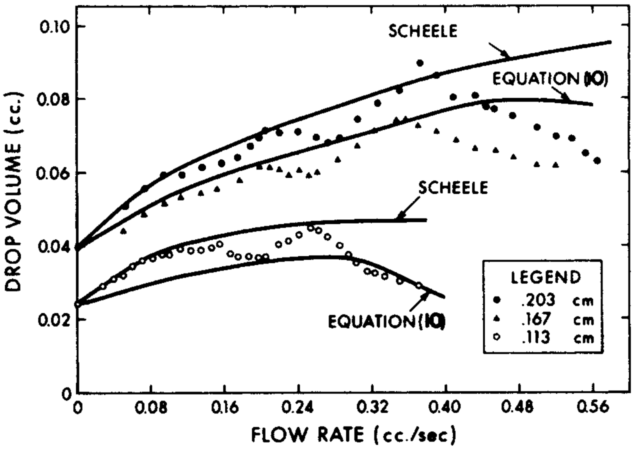

Fig. 4. MIK-water system.

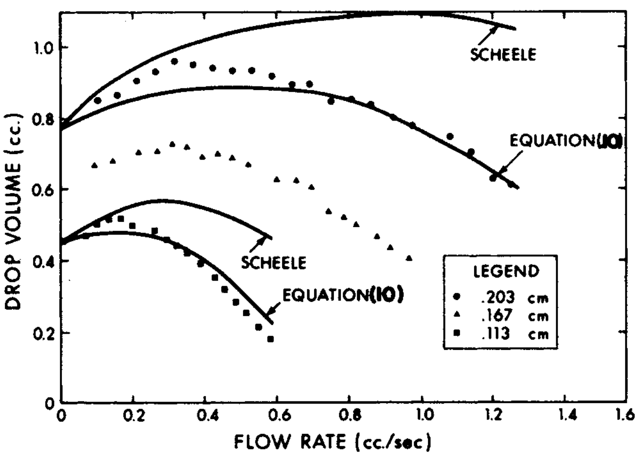

Fig. 5. Phenetole-water system.

NOTATION

C_1, C_2, C_3, = constants defined in the text
D = diameter, cm.
g = gravitational constant
m = mass, g.
Q = flow rate, cc./sec.
R = radius, cm.
t = time, sec.
U = velocity, cm./sec.
V = volume, cc.

Greek Letters

β = term in Equation (10) as defined in Equation (13)
Ψ = Harkins' correction factor
ρ = density, g./cc.
σ = interfacial tension, dynes/cm.

Subscripts

D = drop
j = jet
N = nozzle
t = terminal, applying to the drop after detachment
1 = first phase of drop formation
2 = second phase of drop formation

LITERATURE CITED

1. Bashforth, F., and H. Adams, "An Attempt to Test Theories of Capillary Action," Cambridge Univ. Press, London (1883).
2. Batson, J. B., M.Sc. thesis, Univ. Tennessee, Knoxville (1951).
3. Christiansen, R. M., and A. N. Hixon, *Ind. Eng. Chem.*, **49**, 1017–1024 (1957).
4. Harkins, W. D., and E. C. Humphrey, *J. Am. Chem. Soc.*, **38**, 240 (1916).
5. Hayworth, C. B., and R. E. Treybal, *Ind. Eng. Chem.*, **42**, 1174 (1950).
6. Hu, S., and R. C. Kintner, *AIChE J.*, **1**, 42 (1955).
7. Null, H. R., and H. F. Johnson, *ibid.*, **4**, 273 (1958).
8. Rao, E., K. Kumar, and N. Kuloor, *Chem. Eng. Sci.*, **21**, 867 (1966).
9. Rayleigh, Lord, *Proc. Roy. Soc.*, **29**, 71 (1879).
10. Ryan, J. T., Dissertation, Univ. Missouri, Columbia (1965).
11. Scheele, G. F., and B. J. Meister, *AIChE J.*, **14**, 9 (1968).
12. Tate, T. T., *Phil. Mag.*, **27**, 176 (1864).

Manuscript received September 11, 1967; revision received August 11, 1969; paper accepted October 7, 1969.

Computerized Catalytic Kinetics: A Useful Extension of the Method of Wei and Prater

E. A. LOMBARDO and W. KEITH HALL
Carnegie-Mellon University, Pittsburgh, Pennsylvania

An extension of the method of Wei and Prater has been devised for determining the relative rate constants for an isothermal, first-order, reversible, three-component system, namely, the catalyzed isothermal isomerization of *n*-butenes. The new method reduces the required work to one experiment.

Wei and Prater (*1*) developed an interesting and elegant method for evaluating the kinetic parameters of monomolecular or pseudomonomolecular, first-order multicomponent systems. Its application, however, has usually required as much experimental work as the classical approach, where the relative rate constants are derived from the initial product ratios. Because of this, and because the mathematics appear forbidding, the method has not been widely used by catalytic chemists, even for those systems where its utility has already been demonstrated, for example, the isomerization of the *n*-butenes. The real value of this work, then, has been that it has clarified the limitations of kinetic studies and has defined exactly what can and cannot be derived therefrom.

The purpose of the present paper is to present a simple extension of this treatment which leads to a great reduction in the amount of experimental work needed to define the system completely. This was done without excessive complication of the computation involved. The new approach was applied to the isomerization of *n*-butenes (a coupled, first-order, ternary system) over a carefully purified Na-Y-zeolite. It is convenient therefore to limit the following discussion to this system.

Faith and Vermeulen (*2*) also developed a method to calculate the absolute rate constants of a three-component system based on the Wei and Prater analysis. This method used only a few points of a single-reaction path and involved a graphic matching of experimental points to a master plot which had been previously constructed. In order to improve its accuracy, it would be necessary to apply curve fitting techniques to the graphic step, to increase the number of experimental points, and, perhaps, to apply an iterative method to the results obtained from the master plots. Although a computer could obviously be adopted for this purpose, a more direct method was derived.