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Mass Transfer and Internal Circulation in Forming Drops

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The presence of internal circulation in forming liquid drops has a significant effect on mass transfer rates. For the systems studied, no circulation was observed below a Reynolds number of 9.7. For Reynolds numbers between 9.7 and 34.4, transition from zero circulation to complete circulation during the entire drop formation period occurred. In studies on the rate of mass transfer from fixed volume drops with forced internal circulation, increases in mass transfer rates were found at Reynolds numbers which corresponded to those observed for the development of internal circulation patterns within the drop.

SCOPE

Internal circulation in drops rising or falling in a second fluid has been studied extensively in recent years. It is caused by shear forces transmitted across the interface as the drop travels. Streamlines for this type of flow were originally derived by Hadamard (1911). Spells (1952) observed and reported such circulating flow, and, since then, it has been studied and photographed by many investigators. Kronig and Brink (1950) derived a model for mass transfer from circulating drops which gave an effective diffusion coefficient two and one fourth times the molecular value and Johnson and Hamielec (1960) have shown experimentally that much higher mass transfer rates occur for circulating than for noncirculating drops as they travel through a continuous phase.

Considerably less work of a quantitative nature has been done on the similar problem of internal circulation in forming drops. Numerous observations of circulation within forming drops under a variety of conditions have been made, and it is generally accepted that, when it exists, internal circulation can make a major contribution to the overall mass transfer rate during drop formation. The purpose of the work reported here was to characterize the nature of the internal flow patterns observed in a forming liquid drop, to study the effect of such motion on mass transfer rates, and to begin to establish quantitative criteria for the conditions under which circulation may be expected in forming drops.

CONCLUSIONS AND SIGNIFICANCE

Ordered flow patterns were observed in forming drops of Varsol mineral oil in a continuous water phase. Over a range of inlet velocities, different for each fluid viscosity, a transition from a pattern of complete circulation during the entire formation period to one in which no circulation occurred during formation was observed. For a fixed nozzle geometry, complete circulation occurred at a Reynolds number of 34.4, and no circulation was found below a Reynolds number of 9.7. Mass transfer studies were carried out with drops of fixed volume formed on a tip to which an annulus had been added so that fluid could be withdrawn from the annulus at the same rate at which it entered through a central orifice. In this fashion, forced circulation patterns were created within the drop. For the forced circulation drops, a rapid increase in mass transfer rates was found as the Reynolds number varied from 10 to 30. This transition range for the increase in mass transfer rates corresponded to the transition range of Reynolds numbers, where internal circulation within the drop developed, and shows the relation between internal circulation and mass transfer in the formation of liquid drops.

The results of mass transfer studies in forming drops reported by other investigators show that in many cases where the Reynolds numbers can be calculated from the data given, reports of high or low mass transfer rates agreed with the Reynolds number criteria found in this work. Where an increase in transfer over a range of conditions was reported, the calculated Reynolds numbers fell in the transition range of 10 to 30 as reported here.

Since this Reynolds number range was established by varying the viscosity and the inlet velocity of the fluid for drops formed on a nozzle of fixed geometry, more work involving drops of different sizes formed on nozzles of different geometries and wetting characteristics is needed before the criteria presented can be accepted as fully general. However, the agreement with mass transfer results reported for drops over a wide range of sizes suggests that such further work may not change the criteria greatly.

Mass transfer during drop formation was first studied to determine end-effect corrections for absorption and extraction measurements in spray columns. The approach used was to measure the overall transfer of solute for drops rising in columns of various heights and then to extrapolate the results to zero height to obtain the contribution from drop formation and collapse. Interest was further generated by the conflicting results obtained by different investigators who used this technique and reported values ranging from 5 to 45% for the amount of extraction during formation and coalescence in single drop extraction columns (Sherwood et al., 1939; Licht and Conway, 1950; West et al., 1951).

In later work, transfer during drop formation was measured by Coulson and Skinner (1952) and by Popovich et al. (1964) by forming a drop on a tip and then withdrawing it. Mass transfer during the formation period was found by using different withdrawal times and by extrapolating to zero withdrawal time.

More direct methods were used by Groothius and Kramers (1955), who calculated instantaneous mass transfer coefficients from continuous measurements of sulfur dioxide absorption in water droplets as they were being formed, and by Rajan and Heideger (1971), who measured the transfer of ethyl acetoacetate into a continuous water phase as the organic droplets were forming. Both of these direct measurement techniques utilized two-component systems in which one phase was diffusing into the other. There was no third component involved.

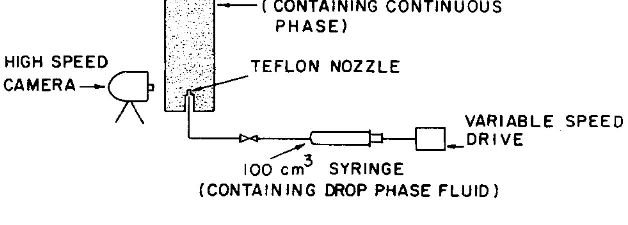

Fig. 1. Diagram of equipment used for measuring internal circulation in forming liquid drops.

Most authors who have studied mass transfer in forming drops have observed the motion which often exists inside the drop as it forms and have indicated at least qualitatively that such motion surely affects the mass transfer rates. Dixon and Russell (1950) were the first to provide a quantitative interpretation of the effect. They used water drops formed on small glass tips of varying internal and external diameters to absorb carbon dioxide and defined a degree of turbulence as being the reciprocal of the inner diameter of the formation tip. Using formation time as a parameter, they found a straight line correlation between the degree of turbulence and the mass transfer coefficient for sixteen formation tips of different sizes.

In work specifically designed to investigate quantitatively the effects of internal circulation on mass transfer rates in liquid drops, Constantan and Calvert (1963) used a tip of two concentric tubes to create a drop with a controlled amount of internal circulation. Fluid entered the drop through the center tube and was continuously withdrawn through the annulus. In the first paper, the results of sulfur dioxide absorption in water and various organic liquids were reported. An effective diffusivity was calculated which would give the correct mass transfer rates if used in place of the molecular diffusivity in a film theory model. A plot of the log of the difference between the effective diffusivity and the molecular diffusivity against the log of the Reynolds number based on the inner diameter of the nozzle yielded a straight line correlation for high Reynolds numbers in the range of 50 to 400.

In a second paper (Panno and Calvert, 1965), which was a continuation of the earlier work, the data were correlated by a plot of the Sherwood number against a Reynolds number based on the flow of liquid along the interface of the drop by assuming that the incoming fluid rose to the apex of the drop and was then deflected equally in all directions along the underside of the interface. The resulting correlation was of the same form and magnitude as that for laminar boundary layer flow in one direction on a flat plate. The range of Reynolds numbers used, based on the inlet nozzle diameter, was approximately 20 to 220.

The latter two papers are unique in that they studied circulation at Reynolds numbers significantly higher than those encountered in all the previous work for which values were stated or could be computed from the information given, with the exception of Dixon and Russell (1950) whose work extended to a value of approximately 175. It is also important that in the first paper the correlation failed below a value of about 50 and that in the second paper the correlation for values less than 50 had a different form from that obtained for higher Reynolds numbers.

In the present paper, the internal circulation patterns for forming and separating liquid drops for inlet Reynolds numbers less than 50 have been studied and, from a fixed volume drop formed on a tip having a concentric tube arrangement for addition and withdrawal of fluid in the same fashion as that used by Constantan and Calvert (1963), mass transfer rates for inlet Reynolds numbers less than 50 were measured.

INTERNAL FLOW PATTERNS

Experimental

A diagram of the experimental apparatus used to study the motion of the fluid in a forming liquid drop is shown in Figure 1. Drops were formed on a teflon nozzle which had an outer diameter of 9.52 mm and an inner diameter of 1.40 mm. Dispersed phase was injected into the nozzle from a hypodermic syringe mounted on a variable speed infusion pump so that the flow rate of the fluid entering the drop could be closely controlled. For studies of the internal flow patterns of a forming drop, the dispersed phase consisted of mixtures of mineral oil and Varsol in the ratios shown in Table 1 to give ten different fluids with a viscosity range of 9.6×10^{-4} to 8.26×10^{-3} N s/m^2 as measured with a Hoeppler falling ball viscometer. The continuous phase was distilled water saturated with Varsol. No mass transfer took place between the two phases.

Aluminum powder was mixed with the drop phase so that the motion of the fluid inside the drop could be followed. To minimize the effect of gravity on the aluminum particles used, the heavier particles were allowed to settle, and the top portion was then decanted off and used to fill the syringe.

As the drops were formed they were photographed with a pin registered Milliken DBM-5 motion picture camera operated at a speed of 200 frames/s. The nozzle was illuminated by two photoflood lamps, one on each side of the drop. Pictures were taken of forming and separating drops for a wide range of dispersed phase flow rates for each of the ten different mineral oil-Varsol mixtures and the resulting film studied to characterize the nature of the motion inside the drops.

Results of Internal Flow Studies

Definite flow patterns were observed in each drop. Over a critical range of inlet velocities which was different for each fluid viscosity there was a transition from a pattern of complete circulation during the entire period of drop formation to one in which no circulation occurred. At high velocities, much of the incoming fluid rose in a column from the nozzle orifice to the apex of the drop, impinged against the apex, and then flowed tangentially along the underside of the interface until it reached a point near the base of the drop. From there some of the fluid was recirculated by being caught up with the fresh stream rising through orifice. A toroidal flow was observed inside the drop with a plume of fresh liquid rising up the center as shown in Figure 2*a*. This type of motion existed during the entire formation period of the drop and is the type of flow pattern assumed by Constantan and Calvert (1963) in their study of internal circulation.

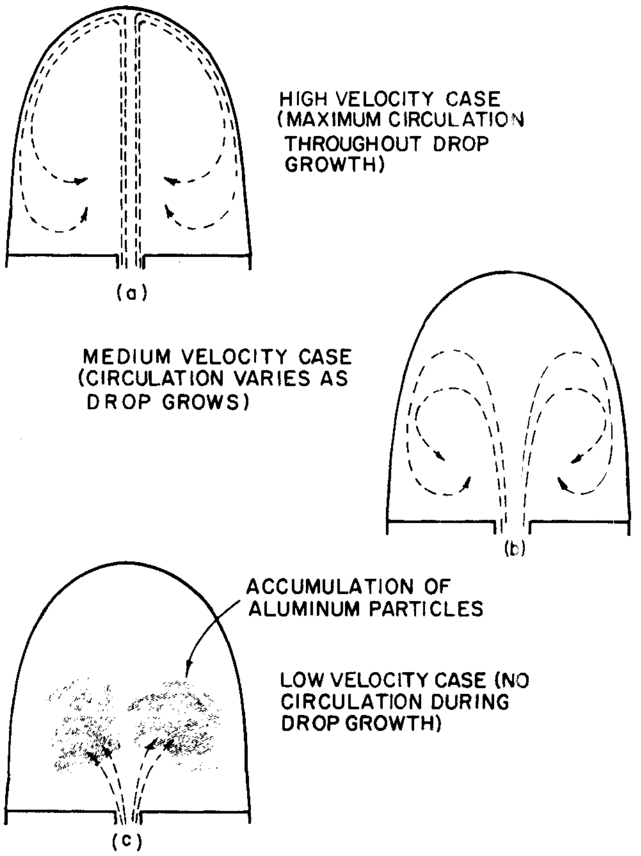

Fig. 2. Internal flow patterns observed in forming liquid drops at different inlet velocities.

As the inlet velocity was decreased, a point was reached at which the flow pattern began to change. During the early stages of growth, flow within the drop was the same as that observed at higher velocities. However, as the drop grew larger the column of entering fluid began to spread noticeably because of dissipation of the momentum of the fluid. During the later stages of growth the incoming stream no longer reached the apex. As a result, circulation did not occur throughout the entire drop for the complete formation period. This condition is illustrated in Figure 2b.

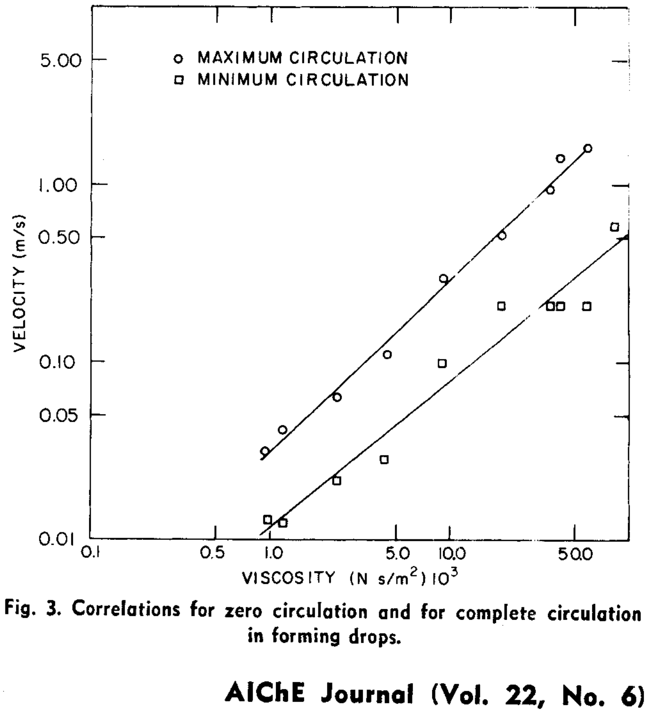

Fig. 3. Correlations for zero circulation and for complete circulation in forming drops.

Table 1. Formation Data for Mineral Oil-Varsol Drops of Low, Medium, and High Viscosity

Fluid (min. oil: Varsol)	Density (kg/m^3)	Viscosity ($N\ s/m^2$) 10^3	Velocity (m/s)	Flow rate (cm^3/s)	Total formation time (s)	Growth time (s)	Percent* complete circulation	Reynolds† number
1:0	865	82.62	0.579	0.89	2.88	2.62	0	8.5
			0.965	1.48	2.53	2.20	25	14.1
			1.276	1.96	2.26	1.98	28	18.9
			1.616	2.48	1.02	0.84	45	28.6
20:1	861	59.69	0.208	0.32	3.31	3.13	0	4.2
			0.684	1.05	1.08	0.90	47	13.8
			1.276	1.96	0.89	0.72	63	25.7
			1.616	2.48	0.71	0.55	100	32.6
10:1	858	41.03	0.208	0.32	5.85	5.55	0	6.1
			0.431	0.66	1.63	1.47	41	12.6
			0.684	1.05	1.02	0.88	61	20.0
			0.965	1.48	0.97	0.83	67	28.2
			1.276	1.96	0.78	0.61	82	37.2
			1.409	2.16	0.66	0.50	100	41.2
8:1	856	36.55	0.208	0.32	2.90	2.81	0	6.8
			0.431	0.66	1.28	1.13	64	14.1
			0.684	1.05	0.91	0.76	79	22.4
			0.965	1.48	0.67	0.51	100	31.6
4:1	849	19.46	0.208	0.32	3.05	2.84	0	12.7
			0.338	0.52	1.70	1.51	66	20.6
			0.431	0.66	1.10	0.91	92	26.3
			0.529	0.81	0.82	0.64	100	32.2
2:1	838	9.19	0.100	0.19	11.41	10.88	0	15.8
			0.208	0.32	2.91	2.01	74	26.5
			0.294	0.45	1.40	1.19	100	37.5
1:1	824	4.44	0.031	0.04	14.00	13.65	0	6.7
			0.062	0.10	4.37	4.20	43	16.1
			0.086	0.13	3.04	2.78	83	22.3
			0.112	0.17	2.30	2.07	100	29.0
1:2	810	2.37	0 022	0.03	10.00	9.85	0	9.5
			0.042	0.06	5.57	5.42	66	20.0
			0.053	0.08	4.25	4.10	88	25.3
			0.065	0.10	3.55	3.40	100	31.0
1:10	789	1.19	0.013	0.02	13.54	13.41	0	12.0
			0.031	0.05	6.44	6.31	82	28.7
			0.042	0.06	4.75	4.63	100	38.9
0:1	780	0.96	0.013	0 02	15.59	15.44	0	14.8
			0.022	0.03	8.71	8.57	72	25.0
			0.031	0.05	5.96	5.82	100	35.2

* Percent complete circulation $= \dfrac{\text{time of complete circulation}}{\text{growth time}} \times 100.$

† Based on inlet orifice diameter.

Again, for the same fluid but with a further decrease in the inlet velocity, circulation caused by the incoming fluid was negligible throughout the entire formation period. The aluminum particles entering the drop rose only a short distance before viscous effects stopped their upward motion. The particles accumulated in the lower part of the drop indicating that the fresh fluid was staying at the bottom and pushing the older fluid upward without any appreciable circulation. The upper part of the forming drop consisted of a large cap of stagnant fluid as shown in Figure 2*c*.

The internal behavior of drops formed with each of the ten different dispersed phase fluids was analyzed by projecting the high-speed photographs onto a large rear projection screen and by following the motion of the aluminum particles inside the drop. For purposes of analysis, the total formation period was divided into two stages defined as a growth stage and a separation stage. The dividing point between these two stages was chosen as the point at which necking-in appeared. By observing the motion pictures, the beginning of the separation stage could be determined within one or two frames of film, giving an accuracy of 1 to 5% relative to the total formation time.

For the least viscous fluid (9.6×10^{-4} N s/m²), no observable circulation occurred below an inlet velocity of 0.0126 m/s, and complete circulation during the entire growth stage was observed at velocities greater than 0.0314 m/s. The velocity range over which this transition took place for the most viscous fluid studied (82.62 centipoise) was 0.208 to 1.616 m/s. The transition velocity range for fluids with intermediate viscosities fell within these limits. A plot of the velocity required for complete circulation during the entire formation period against the corresponding fluid viscosity is given in Figure 3. The data best fit a power curve relationship for which the equation is

$$v = 26.08\mu^{0.97}$$

The Reynolds number for complete circulation was nearly constant at 34.4 ± 4 over the range of the experimental data. For the smoothed data it was 34 ± 0.5.

The experimental velocities at which little or no circulation occurred are also plotted in Figure 3. The data for this case are much more scattered, the scatter resulting from difficulty in determining the amount of circulation during the early stages of drop growth because of oscillation produced by separation of the previous drop. A power curve was also used to fit these data. The equation is

$$v = 3.65\mu^{0.83}$$

For this case, the Reynolds number computed from experimental data was 9.7 ± 3.9 and, from the curve in Figure 3, it was 9.5 ± 2.3.

These results show that an ordered flow pattern does exist in a forming liquid drip and that for a given nozzle geometry the conditions at which circulation ceases and at which complete circulation during the formation period occur are functions of the Reynolds number based on the inlet nozzle diameter.

The above results have been limited to the formation stage of the drop. The motion of the aluminum particles was also followed during the drop separation stage. As the neck of the drop began to contract, the entire mass of the drop above the neck assumed a vertical motion, and there was no circulation even through flow continued from the nozzle. This observation is similar to that reported by Halligan and Burkhart (1969) for a separating drop with no incoming fluid.

MASS TRANSFER STUDIES

To examine the effect of different amounts of internal circulation on mass transfer rates in liquid drops, the experimental equipment was modified by adding an annulus at the base of the formation tip so that fluid could be withdrawn from the drop through the annulus at the same rate at which it entered through the center, as shown in the drawing in Figure 4. The orifice diameter was 1.40 mm and the outside diameter of the formation tip was 13.74 mm. The annulus used for withdrawal of the dispersed phase had an inside diameter of 9.52 mm and an outside diameter of 10.92 mm. Hypodermic syringes were mounted back to back on the infusion pump so that liquid was fed to the drop through the center orifice from one syringe and withdrawn through the annulus by the other syringe. Since both syringes were the same size and driven by the same pump, the rate of addition and withdrawal was very nearly equal. Small differences in flow rates were compensated for by adjustments on the infusion pump. Thus a drop of constant volume could be maintained over an extended period of time.

Experimental

A drop phase of mineral oil and cyclohexane mixed in different proportions gave a range of viscosities from 8.8×10^{-4} to 5.10×10^{-3} N s/m^2. Acetic acid added in a concentration of 6% by volume provided a solute which would transfer into a continuous phase of water saturated with cyclohexane. For each different fluid mixture, flow rates were chosen so that flow patterns from no circulation to complete circulation were obtained. The flow patterns could be seen without the addition of aluminum particles, since the solute concentration differences within the drop caused differences in the refractive index of the fluid.

For each flow rate used, the equipment was started, the exit flow manipulated to produce a drop of constant size and of equal volume for each run, and the drop maintained on the nozzle for a sufficient time to assure that steady state had been reached. After the run was stopped, a sample of liquid from both the inlet line and the withdrawal line was then taken and analyzed by titration with sodium hydroxide to a thymol blue end point.

Results of Mass Transfer Studies

Mass transfer data for low and medium viscosity fluids are plotted in Figure 5 as percent acid extracted against the Reynolds number based on the diameter of the inlet nozzle to produce the S shaped curve shown in the figure. Below a Reynolds number of 10 there was no apparent change in the mass transfer rates. This corresponds to the value of 9.5 below which no internal circulation was observed in the flow pattern studies. This fact was also confirmed by visual observation of the fixed volume drops during the mass transfer works.

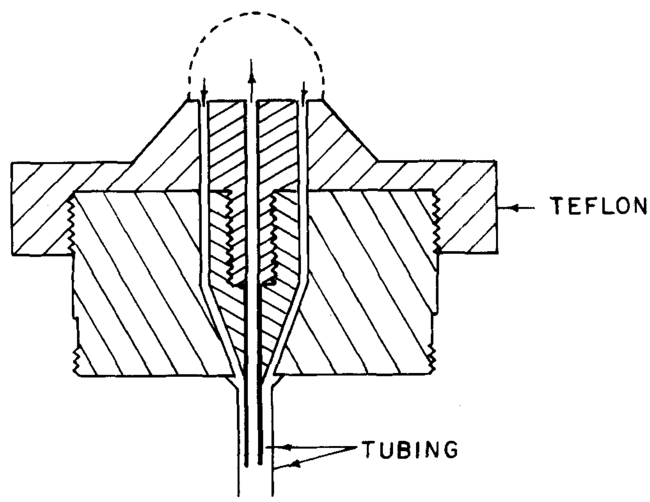

Fig. 4. Modification of drop nozzle to permit forced circulation in a liquid drop.

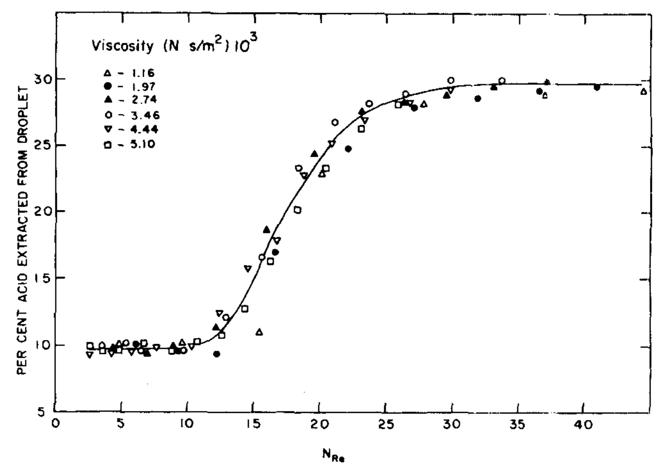

Fig. 5. Mass transfer as a function of Reynolds number for drops with forced circulation.

Mass transfer rates then increased markedly over the range of Reynolds numbers from 10 to 30. The amount of circulation in the drop could be observed visually, and the increased mass transfer rate corresponded to an increase in the internal circulation. Maximum extraction rates occurred very near the flow rates at which complete internal circulation took place. A further increase in the inlet velocity from that required for complete circulation to the velocity at which the drop surface became unstable because of impingement of the jet of incoming fluid against the apex produced only a small increase in the mass transfer rate.

Complete circulation occurred in the fixed volume drops at a Reynolds number of about 30, whereas it occurred in the forming and detaching drops at a Reynolds number of 34. This result is consistent with the fact that a higher velocity is needed to assure complete circulation during the entire formation period of a growing drop since its height at the end of the formation period is greater than that for a stable drop of fixed volume.

Time exposure photographs of fixed volume drops with forced internal circulation are shown in Figure 6 for com-

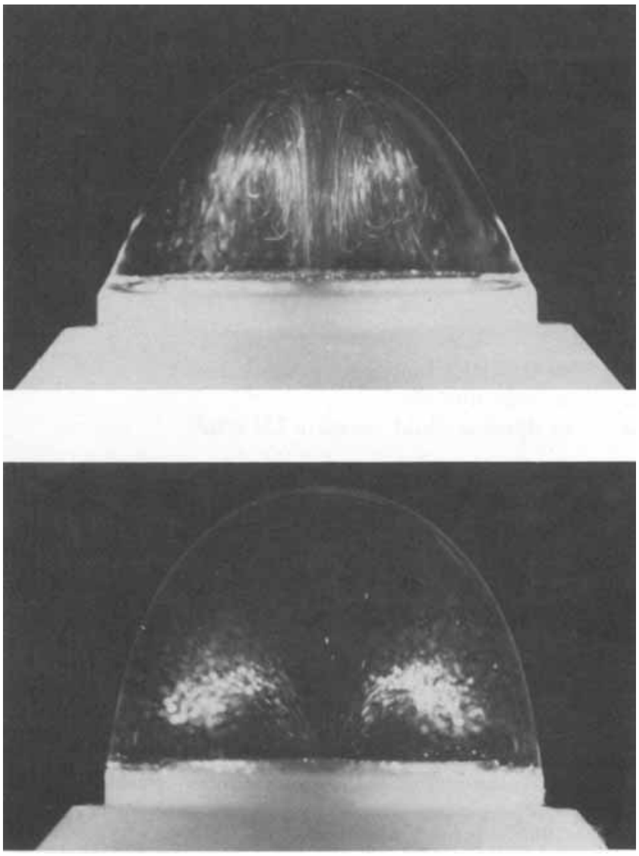

Fig. 6. Time-exposure photographs of aluminum tracer particles showing complete circulation and zero circulation in liquid drops formed on a nozzle.

plete internal circulation and zero internal circulation, respectively. The flow patterns for each case can be seen from the streaks made by aluminum tracer particles in the fluid.

The results of the mass transfer studies show clearly that the mass transfer rate from a drop is closely related to the amount of internal circulation which exists and that once complete circulation is achieved, further increases in the mass transfer rate with increasing Reynolds numbers are much more gradual.

DISCUSSION OF RESULTS

Although the volume of the drops used in this study are quite large compared to drops which have been used by many previous investigators for studying mass transfer during drop formation, qualitative reports of flow patterns similar to those described here have been reported for drops formed on smaller tips. Heertjes et al. (1954) provide a description of such flows from observation of isobutanol drops containing cobalt chloride formed in an isobutanol-water system. The color change from blue to pink as water transferred into a drop was used to show that drops formed on a 6 mm tip containing a 1 mm orifice displayed a marked circulation for formation times of 1.3 s or less, whereas for formation times greater than 1.5 s no circulation occurred.

For formation times less than 1.5 s, a pink zone was found in the lower part of the drop in which a vertical thin blue channel lying in the axis of the nozzle was visible. The upper part of the drop was blue with the exception of a very thin pink film at the interface. During the formation period, the dividing plane between the blue and pink zones moved upward with a velocity dependent on the velocity of formation.

Garner et al. (1955) also reported a qualitative observation of the development of internal circulation patterns in drops formed on the tip of a 25 cm^3 pipette. With the aid of aluminum particles suspended in the drop, they were able to observe the development of the internal circulation patterns in the drops as a function of formation rate. At very slow rates (1 to 2 drops/min), no circulation was seen. At rates of 10 to 30 drops/min, partial circulation was found, and at high formation rates (30 to 45 drops /min), a full toroidal pattern surrounding a thin jet in the center was observed.

The study of forming drops is very system dependent and is a function of many variables. Hence direct comparison of this work with other results obtained for different tip geometries and operating conditions should be approached with some caution. It is possible, however, to compare various studies with this one and to examine the probable effect of circulation upon the previous results. To this end the compilation of velocities, flow rates, formation times, and Reynolds numbers shown in Table 1 was prepared.

Although their drops were smaller, Heertjes et al. (1954) used an inner to outer tip diameter ratio of 0.167 which compares favorably with the value of 0.147 used by the present authors. For fluids with a viscosity of 3×10^{-3} to 4×10^{-3} N s/m^2, their observation of internal circulation for formation times of less than 1.5 s compares well with the value of 2.3 s shown in Table 1 for complete circulation with a fixed viscosity of 4.44×10^{-3} N s/m^2.

Coulson and Skinner (1952) reported that mass transfer during formation was independent of the time of formation for formation times of 0.5 to 1 s when extracting benzoic acid from benzene drops in a continuous water phase. For fluids in the same viscosity range as benzene, the results in Table 1 show that complete circulation occurred for formation times of less than 3.5 s. This observation, coupled with the results in Figure 5 which show a much smaller increase in mass transfer rate with inlet velocity once complete circulation has been achieved, suggests that complete circulation existed for the entire range of formation times studied by Coulson and Skinner. As a result, only the time of exposure and not the change in internal circulation rate would have affected the amount of transfer in the range of their study. It is therefore doubtful that a variation of 0.5 to 1 s in the formation time was sufficient to have allowed any change in mass transfer to be detected.

Groothuis and Kramers (1955) studied the absorption of sulfur dioxide into water from a pure sulfur dioxide environment. In this case, the effect of internal circulation would be to improve the mass transfer rates by transporting dissolved sulfur dioxide away from the gas-liquid interface more rapidly. Resistance to mass transfer in their system was on the liquid (droplet) side of the interface. Using two different formation tips with inner to outer diameter ratios of 0.32 and 0.13 and liquid viscosities from 7×10^{-4} to 3.3×10^{-3} N s/m^2, they found that absorption began to increase as a result of internal circulation at a Reynolds number of 40 to 50.

In a similar study of carbon dioxide absorption, Dixon and Russell (1950) observed an increase in absorption by liquid droplets at a Reynolds number of about 50. Both of these results are generally supported by the present work where, for a viscosity range of 1×10^{-3} to 3×10^{-3} N s/m^2, complete circulation occurred at Reynolds numbers of 30 to 35.

In a more recent but somewhat different type of work, Rajan and Heideger (1971) measured instantaneous mass transfer rates during drop formation using a two-phase system of ethyl acetoacetate drops forming in a continuous water phase. There was no solute to be transported to the interface since the transfer rates were based upon the dissolution of the ethyl acetoactate itself into the water phase. Thus the effect of any circulation in the forming droplet had to have been due to the transmission of shear induced motion across the interface and into the adjacent water phase where the mass transfer resistance was located. Using a tip made of 20 gauge hypodermic tubing with an inside to outside diameter ratio of 0.66, they found that over a Reynolds number range of 11 to 43, the instantaneous mass transfer coefficients were initially very high but fell rapidly and then leveled out as the drop continued to form.

Their interpretation was that this result implied a strong effect of internal circulation which was most important during the early stages of formation when the drop size was smallest. They did not, however, report any observations or measurements on the extent of the circulation in their drops. The viscosity of the drop phase was 1.38×10^{-3} N s/m^2. For a similar viscosity, the results in Table 1 indicate that transition from no circulation to complete circulation occurred over a Reynolds number range of 12 to 40 which is almost identical to the range reported by Rajan and Heideger and represents the Reynolds number range over which complete circulation would occur early in the life of the forming drop but not near the end of the formation period. The agreement is striking and strongly supports Rajan and Heideger's interpretation of their work.

Since they used only a two-phase system without a distributed solute, their work combined with that presented in this paper also shows that in addition to its importance in providing bulk transport of solute to the interface, internal circulation also plays an important role during drop formation in transmitting motion to and across the interface through viscous shear and that this phenomenon can have a pronounced effect upon the continuous phase resistance, a situation encountered in the reverse direction for shear induced circulation in a rising or falling drop.

The same authors also found that at a fixed flow rate of 1.3×10^{-2} cm^3/s, there was little difference in the instantaneous mass transfer coefficients for drops forming on tips of 18 and 20 gauge hypodermic tubing. In both cases the coefficients were high at the beginning of formation and leveled off near the end. But for a larger 16 gauge tip, the curve of instantaneous coefficient vs. time was much lower and almost flat, displaying no high initial value. Reynolds numbers for the 20, 18, and 16 gauge tips were calculated as 21.4, 15, and 10.5, respectively, using data given in their paper. They reasoned that the anomalous curve for the large tip must have been the result of very little circulation in the drop. This conclusion is also supported by the data in Table 1, where no internal circulation was found at a Reynolds number of less than 10 but that at values of 15 to 20 circulation took place during about half of the formation period.

Finally, the work of Constantan and Calvert (1963) and Panno and Calvert (1965) should be examined closely because they used the same technique for measuring the effect of internal circulation on mass transfer as was used in this work, except that theirs was a gas absorption system. In the first paper, their correlation for mass transfer in terms of the difference between the molecular diffusivity and an effective diffusivity plotted against the inlet Reynolds number gave a good correlation at Reynolds numbers greater than 50 but failed for values less than 30. They commented that at low Reynolds numbers it was possible that their model was not applicable. The data in Table 1 seem to confirm this since for the viscosity of the fluid which they used (propylene glycol, 0.036 N s/m^2), the internal flow pattern changed from incomplete to complete circulation at a Reynolds number of 30.

Since much of the initial impetus for studying mass transfer during drop formation came from the early papers of Sherwood et al. (1939), West et al. (1951), and Licht and Conway (1950) it is unfortunate that, in retrospect, the papers do not give sufficient information on nozzle diameter and flow rates that the conditions of internal circulation could be calculated. It is quite conceivable that the large differences which they reported in mass transfer during the formation period could have been explained by the presence or absence of such motion in their drops.

NOTATION

N_{Re} = Reynolds number (dimensionless)
v = velocity (m/s)
μ = dynamic fluid viscosity (N s/m^2)

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