Liquid Extraction During Drop Formation: Effect of Formation Time

This study was designed to evaluate the effects of internal droplet convection on the extraction that occurs during generation of a dispersed phase. A photographic determination of dispersed-phase controlled mass transfer from liquid droplets in the formation stage demonstrates a strong dependence on formation time. Convection appears to control mass transfer during rapid drop formation, but an abrupt transition in transfer coefficient occurs as time of formation increases. Diffusion calculations overestimate total extraction for long formation times.

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Introduction

The transfer of mass between liquid drops and a surrounding immiscible liquid phase provides the basis for industrial extraction operations, where appropriate design of equipment requires a fundamental understanding of the mechanisms of transport between dispersed and continuous phases. Theoretical and experimental attention has already been given to the development of mathematical as well as descriptive models of the extraction process, where the systems studied have ranged from individual drops to the multidrop clusters appropriate to full-scale equipment. It has generally been accepted that all drops experience three distinct, different length periods in their existence:

1. Formation, detachment, and acceleration to steady velocity
2. Free-fall or rise
3. Coalescence.

It is not uncommon for an investigation to focus on an individual stage in the drop lifetime in order to eliminate competing effects that could mask the fundamental mechanisms of mass transfer involved. Single-drop studies have frequently concentrated on mass transfer and drop dynamics in the free-fall period, with less attention given to formation and coalescence; experimental studies are thus often designed to eliminate the mass transfer in these latter stages, or to evaluate it as an end effect by some extrapolation procedure.

The importance of the drop formation process was suggested many years ago by authors such as West et al. (1951), who found that end effects accounted for a significant fraction of the mass transfer in their study. The various mathematical models developed for mass transfer during drop formation are generally based on a solution to the diffusion equation without any allowance for circulation within the drop; the differences in treatment have involved the methods used to account for introduction of new area to the surface of a growing drop. The two most widely accepted calculations, which have frequently been used for data correlation, invoke the assumptions either of surface stretch (Ilkovik, 1934; Michels, 1960; Angelo et al., 1966; Ruckenstein and Constantinescu, 1969) or of the introduction of fresh elements into the surface (Groothius and Kramers, 1955). These approaches and others have been summarized by Popovich et al. (1964) and by Walia and Vir (1976). When the drop is taken to be a sphere growing at a uniform rate, the time dependence of surface area may be written as:

$$A = \pi \, d_f^2 t_f^{-2/3} t^{2/3}. \tag{1}$$

The predictions of the several models for cumulative mass transfer are numerically different but all suggest the same dependence on physical parameters and the same exponent in the time dependence:

$$N_A = (\text{constant})(C_S - C_o)(D\pi)^{1/2} \, d_f^2 t_f^{-2/3} t^{7/6}. \tag{2}$$

Predicted values for the constant in Eq. 2 are 1.31 for the assumption of surface stretch and 1.52 for fresh surface. Using an innovative formation-withdrawal technique to evaluate drop formation mass transfer, Popovich et al. (1964) tested the various models represented by Eq. 2 and determined that the surface-stretch approach best fit their results. Heertjes and DeNie (1966), however, employing a short column to minimize mass transfer following formation, obtained results more consistent with the fresh-surface calculation.

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Rapid drop formations must of necessity result in internal drop circulation, which will then strongly influence the mass transfer observed (Heertjes et al., 1954; Zimmerman et al., 1980). In an early photographic study of drop formation (Rajan and Heideger, 1971), we reported a significant effect of internal convection on measured mass transfer coefficients, even though the transfer was continuous phase resistance controlled. Subsequently (Heideger and DuBois, 1985), we demonstrated a similar effect for the dispersed phase resistance and showed that in both cases the mass transfer coefficient averaged by integration over the formation period was well correlated with the total drop formation time. Limits for the influence of circulation were not established, however, and internal circulation may effectively cease before drop detachment (Humphrey et al., 1974a) when formation times are long. Thus the linear semilogarithmic dependence of average coefficient for a given drop on the formation time for that drop must eventually break down.

The present study was undertaken to examine the mass transfer coefficient over a wide range of formation times such that internal drop convection should be important for rapid formation rates and relatively insignificant for slow rates. Any conversion from a circulating to a stationary drop will dramatically decrease the mass transfer potential during formation. This experimental study then evaluates the convective control of drop formation mass transfer over such a range of formation times that the transition from circulating to stagnant drops is expected. Dispersed phase resistance is selected to maximize the effect of droplet circulation, and formation times are then extended to the point that all circulation should cease. A photographic technique is used for direct measurement of mass transfer to eliminate any need for extrapolation during data reduction. A qualitative description is formulated for the mass transport mechanisms regulating extraction rate during drop formation. Experimental work is focused on convective vs. diffusive control of transfer rates and on evaluation of the decay of the instantaneous mass transfer coefficient as internal circulation is damped.

Two distinct time regimes are observed, with unique dependencies of the average mass transfer coefficient on formation time. It appears that in rapid formation, internal convection decreases during drop growth but never completely ceases. The inverse dependence of (log) average coefficient on formation time is very strong, since both the initial level of circulation and the degree to which that motion is damped depend on formation rate. In slow formation, the average coefficient continues to decline with increasing formation times, but at a much slower rate. All internal motion appears to have ceased before final drop detachment in these cases and the slow transport attributable to molecular diffusion becomes the dominating factor at very long formation times. In all slow formations, however, mass transfer predictions of diffusion-based models are found to be considerably higher than the actual observations, suggesting that the penetration models used for calculation assume more effect of drop growth on surface stretch/renewal than is realistically encountered.

Experimental

A two-component, two-phase system was selected for study in order to reduce the number of variables and to localize the mass transfer resistance entirely within the dispersed phase. The continuous phase was 2-ethoxyethyl acetate presaturated with water, and the dispersed phase was water initially containing no organic. The study was restricted to evaluation of the mass transfer during drop growth while attached to a submerged formation nozzle and did not include detachment or any subsequent motion of the drop. Mass transfer data were obtained by a careful determination of the difference between the actual drop volume (as measured from the cine film record of the formation) and the known volume of water that had been introduced into the drop up to the time of measurement, this difference being the amount of organic (plus associated water) extracted by the drop. With cine photography, a nearly continuous record of the mass transferred to the drop is thus obtained.

Apparatus

The equipment required to accomplish the above measurements is shown schematically in Figure 1. Since no mass transfer occurred within the continuous phase, flow of the organic was not required. Water was forced into the forming drops at a carefully controlled rate by the use of a Harvard Apparatus Co. infusion pump capable of delivering a wide range of flow rates with an accuracy of ±0.1%. Heideger and DuBois (1985) have previously shown that measurements with multiple nozzle diameters all correlate with a single line, and thus only one formation nozzle was used for this study. It was made of 18 gauge stainless hypodermic tubing (0.0841 cm ID, 0.125 cm OD), the end of which had been carefully ground flat and deburred to insure symmetric drop formation. Water did not wet the nozzle tip, so the drops were always attached only to the inner nozzle circumference.

The camera used was an Arriflex 16 mm cine camera fitted with a Kilfitt Makrokilar 90 mm lens providing film images that were essentially life-size. Light from a 150 W reflector lamp was filtered through a saturated solution of copper sulfate in water; both Kodak Plus-X negative and Kodak Double-X negative film were used. This technique resulted in drop images characterized by a sharp, dark boundary surrounded by a clear exterior phase. An electric digital timer was placed in the camera field of view so that each film frame contained a record of the time during drop formation. Data reduction from the film was accomplished on a Vanguard Motion Analyzer, where linear dimensions could be measured to ±0.002 in. (0.05 mm) on a 25X magnified image.

Procedure

Water to be used for the dispersed phase was deionized and then twice distilled. Practical grade 2-ethyoxyethyl acetate was

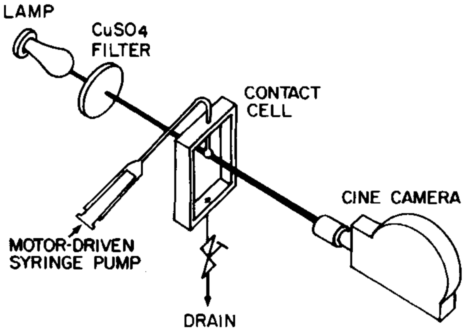

Figure 1. Apparatus.

vacuum distilled twice, mixed with distilled water, and shaken vigorously for the 24 h preceding each run. Prior to each run, all glassware and Teflon gaskets were washed in hot soapy water and soaked in hot chromic acid for several hours. They were then rinsed in tap water, followed by distilled water and reagent grade acetone. Metal parts were treated similarly except that the acid soak was eliminated. The contacting cell was rinsed several times with the organic solution and then filled with 250 mL of the continuous phase. A small pendant drop was formed on the nozzle tip and the camera was focused on this stationary drop prior to the start of drop formation. The lighting, timer, infusion pump, and camera were then activated simultaneously and five to ten drops were photographed at one flow rate. A drop formed near the middle of this series was selected from the film for analysis.

Mass transfer to the drops was determined by analyzing the total drop volume from at least 20 different frames selected at approximately equal time increments during a drop formation sequence. Each of these photographs was evaluated on the assumption that the drop was axisymmetric with respect to the nozzle axis. Along this axis, the drop was divided into 30 segments, each approximating the frustum of a cone, and the drop diameter was measured at the beginning and end of each segment (a measurement of the nozzle diameter was used to set the optical magnification). Surface areas and volumes were calculated for each segment and summed by a computer program which then determined cumulative mass transfer and mass transfer rates. The instantaneous mass transfer coefficients were also calculated from the ratio (Transfer rate, g/s)/(Surface area, cm^2)(Concentration driving force, g/cm^3). A minor complication was introduced by consideration of additions to the drop volume by water forced from the continuous phase, previously saturated with water. It was assumed that as organic was transferred to the drop, the associated dissolved water was also added to the drop volume but did not represent mass transfer between phases. This incremental volume was therefore subtracted before the mass transfer calculations were performed.

Results and Discussion

A total of nine different flow rates and thus nine formation times were investigated. The experimental conditions and the results obtained are summarized in Table 1, where it is evident that the final size at which a drop detaches is not a strong function of its formation rate. Figure 2 shows the time-averaged mass transfer coefficients calculated for each total formation time, plotted as suggested by Heideger and DuBois (1985). Their measurement of mass transfer coefficients for rapid formation in this system is also shown. Two things are immediately obvious: the present results are quite similar but not identical to the previous study, and there is a dramatic break in the dependence of log k_D on increasing time of formation. The explanation for the apparent discrepancy between experiments is embarrassingly simple; in the former study, we made no correction for an addition to the drop of the water dissolved in the organic continuous phase and thus the numerical values for the coefficient were artificially high. The present case has been adjusted to discount the apparent transfer of water and thus reports only the coefficients for extraction of organic solute into the aqueous drop; without this correction, the present measurements would match the previous results quite well.

Table 1. Summary of Experimental Results

Run No.	Formation Time s	Final Equiv. Sphere Dia. cm	Final Cumulative Mass Transfer µg	Avg. Mass Transfer Coefficient cm/s × 10^6
1	2.52	0.3868	582	4,654
2	4.86	0.3846	378	2,474
3	7.70	0.3606	537	1,147
4	11.06	0.3739	503	997
5	12.30	0.3618	582	1,060
6	15.98	0.3548	529	885
7	19.64	0.3651	639	801
8	21.61	0.3441	494	754
9	32.43	0.3462	749	637

The 95% confidence interval for the regression line fitting the long formation time results is shown in Figure 2. This corresponds to a variability of ±11% in the magnitude of the mass transfer coefficient, which is quite consistent with the estimate by error propagation of a maximum probable error just over 10%. The 95% confidence interval for the short formation time results is indistinguishable from the line itself, which is probably fortuitous since only three data points were obtained. We do not expect any less error in these measurements, and so an 11% uncertainty is probably appropriate here as well.

The sharp break in the line at a formation time of about 7.5 s is assumed to result from some transition in the circulation that occurs within drops during formation. It is certainly too simplistic to assume that all drops formed in the short time region are totally circulating and all drops formed in the longer time region are totally stagnant; we have earlier demonstrated a dramatic decay in the instantaneous mass transfer coefficient for rapid formations, which we conclude corresponds to a decrease in or elimination of circulation prior to drop detachment. Humphrey et al. (1974a) defined a circulation number, the product of modified Weber and Reynolds numbers, as a criterion for transition from circulating to stagnant drops. This number decreases with time during formation for any drop, reaching a minimum value at detachment; we therefore have evaluated the circulation numbers at detachment for the drops formed in this study and find them to range from about 1.0 for the most rapid formation

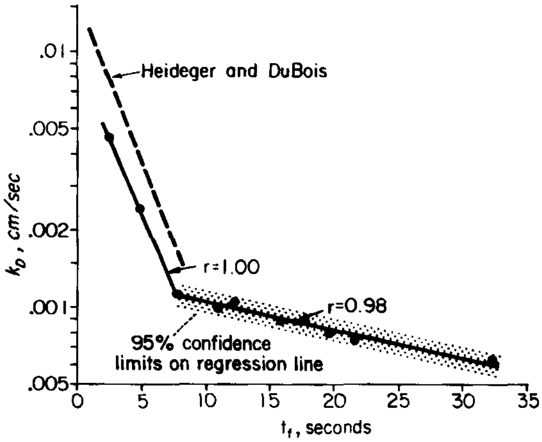

Figure 2. Correlation of average mass transfer coefficient with formation time, dispersed phase controlled.

to less than 0.0001 for the slowest formation. The average criterion suggested for a transition was just less than 1.0, but the measured range was from about 4 to 0.004. This suggests that at least some, and possibly all, drops in this study will have undergone transition to a stagnant condition before leaving the nozzle. It also seems logical to assume that even the slowly formed drops may have experienced some initial limited circulation; although the lowest nozzle Reynolds number was only 0.9, well below the range in which Humphrey et al. (1974b) characterized internal drop velocities. This perspective is substantiated, however, by the time dependence of the instantaneous mass transfer coefficients in the slow formation region. In all cases, the coefficient is high for the initial drop and then rapidly decreases as the drop size begins to increase. The more rapid of these formations have higher initial coefficients, but they then decay more quickly since the drop volume is increasing more rapidly; Figure 3 demonstrates this effect for the two extreme cases in the slow formation region. Note that the decrease from initial to final values of the mass transfer coefficient is more than an order of magnitude, even for a drop that requires over 32 s to form.

We now wish to postulate that the changes seen in Figure 3 result from the combination of two effects, the decay of circulation and the normal increase in diffusional distances within the drop as the size increases. In both cases shown, as in all others from this slow-formation region, the dramatic decrease in coefficient appears to be ended by about 6 to 8 s into the formation period; the later changes are then much more gradual in all cases. Presumably, the early, rapid falloff corresponds to the damping of convection within the drop, and the mass transfer subsequent to this time may then be attributed to molecular diffusion alone. Thus any attempt to fit the observed slow-formation mass transfer results to the diffusion models must be restricted to the time after elimination of any circulation.

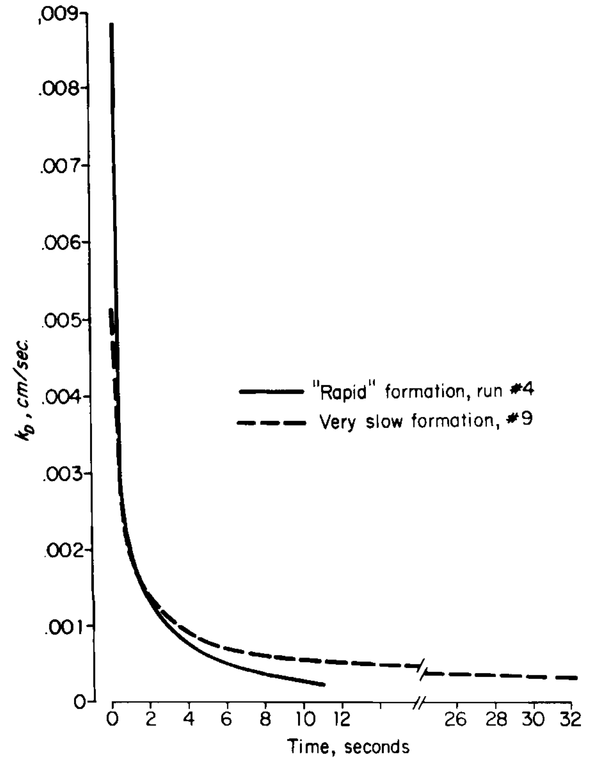

Figure 3. Variation of instantaneous mass transfer coefficients with time, slow-formation region.

To test this hypothesis, we wish to compare the measured cumulative mass transfer in these slow formations to that predicted by Eq. 2, which requires that the drops grow uniformly as spheres with the surface area described by Eq. 1. Figure 4 shows the measured surface areas for the same extreme cases of the slow-formation region; the match to Eq. 1 appears to be more than adequate for both. We have therefore calculated predicted cumulative mass transfer for these cases by both the surface-stretch and the fresh-surface models. A comparison of the predicted values with our measured values is given in Figure 5, where the speculations above do appear to be confirmed. For run 4, which terminates at about the time convective transport should become negligible, the slope of the experimental curve never attains the 7/6 value expected for diffusive transport. The results from run 9, however, appear to be nicely parallel to the model predictions in the latter stage of formation. This may be taken as reasonable evidence that essentially only molecular transport is important at that point in the formation process. However, in both cases the models tend to overpredict the extraction accomplished, even with the early convective contribution in both instances. Thus, some additional modification of the penetration models used to generate Eq. 1 would appear to be necessary.

Still unanswered is the question as to why we obtain the excellent linear relationships for both formation rate regions, as shown in Figure 2. However, the reason for a decrease of the time-averaged coefficient with increased formation time is obvious for both regions. In all cases, the initial level of circulation and therefore the initial mass transfer coefficient must be higher for a higher formation rate (lower formation time). If then, final circulation damping occurs at about the same time into the formation period (as implied by the present results), total damping will not have occurred in any of the rapid formations but the damping will be more nearly complete for the longer formation times. As formation time increases, the initial value of the coefficient will be reduced at the same time that the degree to which it decays is increased, resulting in a very rapid decline of the average coefficient with increased formation time. Once the transition point is reached, however, all drops are presumed to experience total damping of circulation, but the average coefficients for drops with very long formation times will be domi-

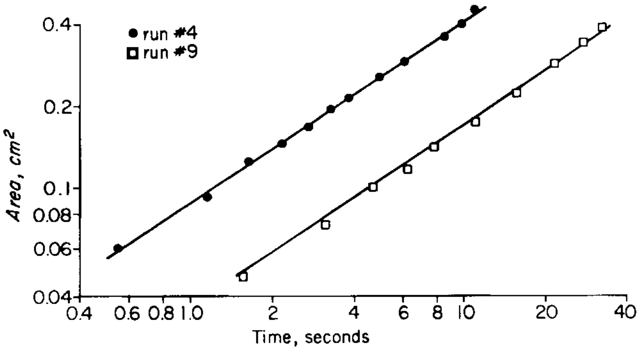

Figure 4. Surface area growth in slow-formation region. Lines predicted by Eq. 1.

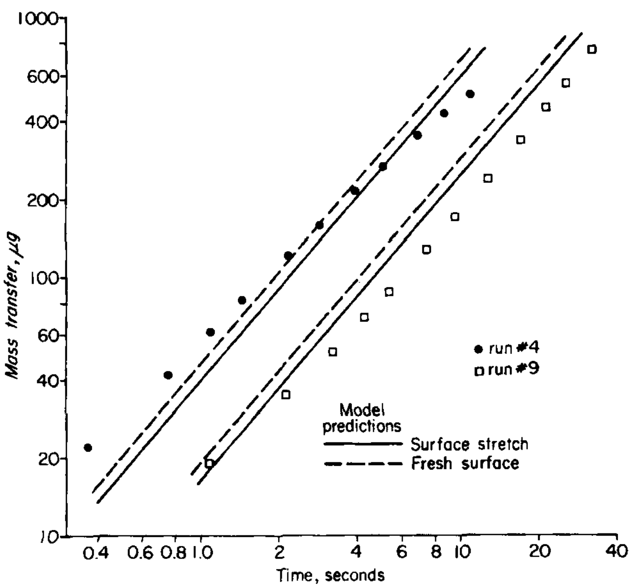

Figure 5. Growth of cumulative mass transfer in slow formation region.
Predictions by Eq. 2.

nated by the low coefficients characteristic of molecular transport. The early convection for a fixed period (but at an initial level that decreases with increased formation time) combines with a variable period of low transport to continue the reduction in average coefficient with increasing formation time, but now at a much slower pace.

Acknowledgment

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Notation

A = surface area of drop, cm^2
C = solution concentration, g/cm^3
C_o = initial concentration
C_S = saturation concentration
d_f = final equivalent spherical diameter
D = diffusivity of solute in dispersed phase, cm^2/s
k_D = mass transfer coefficient for dispersed phase, cm/s
N_A = cumulative mass transfer to drop, g
r = coefficient of correlation, Figure 1
t = time, s
t_f = total formation time for drop

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