Drop Formation Mass Transfer

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The mass transfer occurring between a liquid drop during its formation and the surrounding liquid phase was directly evaluated by a photographic technique. Slightly soluble organic drops containing no additional solute were formed in a continuous aqueous phase so that only the continuous phase resistance existed. Effects of nozzle diameter and both phase flow rates were evaluated and the possible influence of surfactant was investigated.

Mass transfer coefficients were observed to decrease sharply with time early in the formation period. This, together with the parametric study of dispersed phase feed rate, indicates the strong effect of internal drop convection for this high Schmidt number system. The measured coefficients are substantially higher than would be expected for free drops.

In laboratory studies of dispersed phase mass transfer, it has been customary to treat that occurring during drop formation and coalescence as an end effect. Since the purpose of such studies has generally been to characterize mass transfer during the period of free fall, various attempts have been made to eliminate the significance of these end effects or at least their influence on the measurements. In the case of coalescence, this is often not too difficult because of a low driving force and the possibility of restricting interfacial area. However, mass transfer during formation is another matter, since the driving force is at its maximum value during this period. In several instances the total observed mass transfer has been plotted against drop lifetimes and extrapolated to zero contact time to evaluate the effects of formation and coalescence. If the goal is to evaluate mass transfer during formation, however, several difficulties are encountered: it is impossible to distinguish between the two terminal periods and it is necessary to assume the mechanism of mass transfer during acceleration of the drop to its terminal velocity is the same as that during free fall (*7*).

Other attempts to isolate or describe the formation contribution have been made. Of the descriptive models proposed, two have been widely accepted and used for data correlation: the surface stretch (*1*, *6*) and the fresh surface elements (*4*) assumptions. The former requires that a forming drop grow without the addition of fresh dispersed phase material to the interface, while the latter requires growth without distortion of fluid elements within the interfacial region. Popovich, Jarvis, and Trass (*10*) have demonstrated that the various mechanisms proposed in the literature can all be represented by a single mass transfer equation of the form

$$N_A = \text{const}\,(C_s - C_o)\,\sqrt{\frac{D}{\pi}}\;t^{\frac{2n-1}{2}} \qquad (1)$$

in which the initial constant assumes different values for the different models. The exponent arises from the assumption of a time dependence for drop interfacial area of the form

$$A = kt^n \qquad (2)$$

which, for a spherical particle growing at a uniform volumetric rate, becomes

$$A = \pi d_f^2\, t_f^{-2/3}\, t^{2/3} \qquad (3)$$

The measurements of formation transfer rate which they reported were obtained by a refinement of the formation-withdrawal technique in which solute-laden drops are formed at the tip of a syringe and then withdrawn back into the nozzle. Formation and withdrawal times were varied independently and measured mass transfer was extrapolated to zero withdrawal time on the assumption that no transfer would occur with an infinite rate of withdrawal. Based on this data, shown in Figure 1, and the assumption that the mechanism of mass transfer during withdrawal is similar to that during formation, they concluded that the Ilkovic surface stretch model best represented their system. The scatter in such a plot obviously makes it difficult to draw any very firm conclusions. Also, it should be noted that the formation times involved are 1 to 15 sec. with the bulk of the data taken with formation slower than 10 sec. and thus a quiescent, slowly expanding drop might be expected. It is therefore not surprising that a molecular diffusion-based model appears to give an adequate description of the mass transfer results obtained.

A recent study by Heertjes and DeNie (*5*), also with low formation rates but employing a short column to reduce the importance of mass transfer after formation, found the Groothius fresh surface model to be a better representation of observed formation transfer rates. In both these cases, however, the total mass transfer during formation could be correlated with the square root of formation time.

The present study was undertaken to examine mass transfer controlled by the continuous phase resistance during

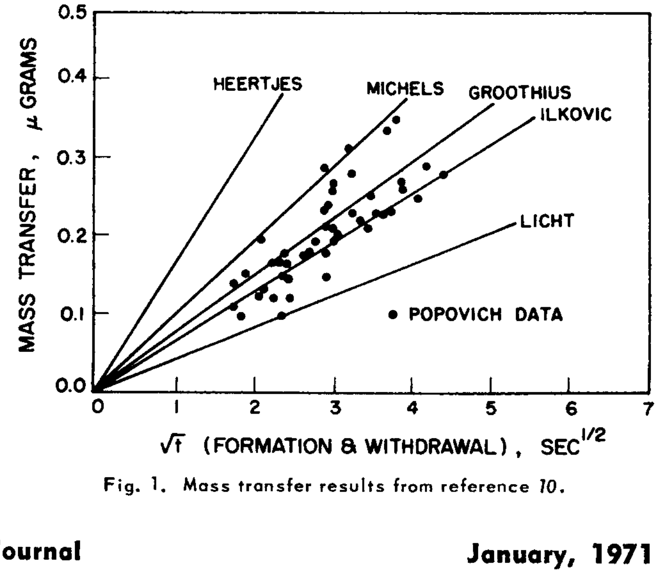

Fig. 1. Mass transfer results from reference *10*.

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formations rapid enough that significant convection might be expected within the drop. It was considered very important that direct measurements of mass transfer be made in order that the need for extrapolation during data reduction might be eliminated. A photographic technique previously refined in this laboratory (*8*, *9*) was selected since it met these requirements and also permitted the evaluation of instantaneous mass transfer rates rather than an integrated average for the entire formation period.

EXPERIMENT

A two-component, two-phase system was selected for study in order to reduce the number of variables. An organic liquid with a water solubility in the range of 10 to 25 wt. % was sought for the dispersed phase and water for the continuous phase. The organic was to be presaturated with water in order that only one-directional transfer would occur with the resistance to mass transfer entirely in the aqueous phase. Ethyl acetoacetate, the physical properties of which are listed in Table 1, was selected as the dispersed phase material.

TABLE 1. PHYSICAL PROPERTIES* OF ETHYL ACETOACETATE (24°C.)

Density	1.022 g./cc.
Viscosity	0.0138 g./(cm.)(sec.)
Diffusivity	1.26×10^{-5} sq. cm./sec.
Interfacial tension	3.5 dynes/cm.
Solubility in water	14.4 g./100 cc.

*As listed in Handbook Chem. Phys. and Int. Critical Tables.

Mass transfer from the drop was to be measured during the period of formation which terminated upon detachment of the drop from the nozzle. The technique for this measurement consists of the following: An organic drop is formed at a known constant volumetric feed rate at the submerged tip of a length of hypodermic tubing. A continuous record of the growing drop dimensions is obtained by cine photography. Because the organic phase dissolves slowly in water, there is always a difference between the total volumetric input to the drop and the instantaneous drop volume as measured from any given frame of the cine film. A careful evaluation of this difference yields the volume transferred up to the time of measurement.

Apparatus

The equipment necessary to accomplish the above measurements consisted of a water supply system, the drop formation apparatus, a phase contacting channel for photography, and associated equipment for taking and analyzing the film record. A schematic diagram of the phase contact arrangement is shown in Figure 2.

The continuous phase is water from the laboratory cold water line which has been passed through a double-bed ion exchanger for dimineralization. The water entering the heat exchanger in the constant temperature bath is comparable in conductivity to triple distilled water. The temperature was adjusted to match room temperature, which was regulated to better than ±0.5°F. From that point the water is metered through the rotameter into the channel. The physical arrangement of the channel is given in Figure 3. The front and back of this channel are plate glass windows and the sides diverge slightly in the direction of flow so that the cross section is square at the inlet but rectangular at the outlet. Silicone rubber gaskets are utilized to seal the windows to the sides because of the minimum potential for contamination by surfactants leached from this material (*12*). Four ports in the channel side allow insertion of the drop formation needle through silicone rubber septa.

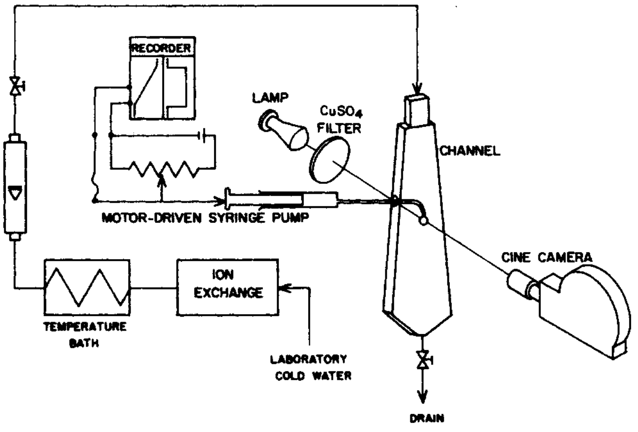

Fig. 2. Apparatus.

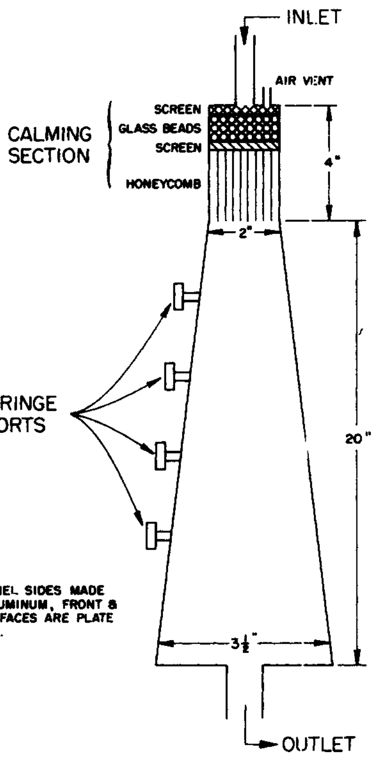

Fig. 3. Phase contact channel.

The flow rate of dispersed material is controlled by a Harvard Apparatus Company infusion pump capable of delivering a wide range of flow rates with an accuracy of ±0.1%. Constancy of the organic feed rate was checked by attaching to the syringe plunger an electrical contact which rode along a resistance slidewire over which a constant voltage was applied. Both the detected voltage and its derivative were recorded on a two-channel high-speed recorder. Since the syringe barrel has a constant cross section, a constant linear velocity of the plunger corresponds to a uniform volumetric flow rate. Drops were formed on three different size nozzles made from 16, 18, and 20 gauge hypodermic tubing. Square ends machined on the nozzles were carefully deburred and made flat with the aid of a fine emery stone. A final inspection of each nozzle tip under a 7× optical comparator was made to determine the absence of irregularities.

The contacting channel was backlighted for photography in a manner similar to that described by Damon (*2*) and Lode (*8*). The cine film was taken with an Arriflex 16S camera equipped with an f/1.4 makrotelephoto lens and extension which permitted close focusing of the lens within 10 cm. from the field. With this arrangement, the drop image was approximately actual size on the film. The camera speed was always 62 frames/sec. and Plus-X negative film was found to give good contrast and fine grain size. Data reduction from the film was accomplished on the Vanguard Motion Analyzer where linear dimensions could be determined to ±0.002 in. on a 25× magnified image.

Procedure

Prior to any run, water was flushed through the channel for at least 30 min. Reagent grade ethyl acetoacetate was redistilled twice and saturated by agitated contact with distilled water for 24 hr. The syringe was cleaned in chromic acid, rinsed with water followed by acetone, and finally air-dried. The syringe was filled and inserted into the pump. A small single drop was formed on the nozzle tip and the camera was focused on this stationary drop prior to the start of drop formation. The infusion pump, camera, and recorder were then started simultaneously and six to

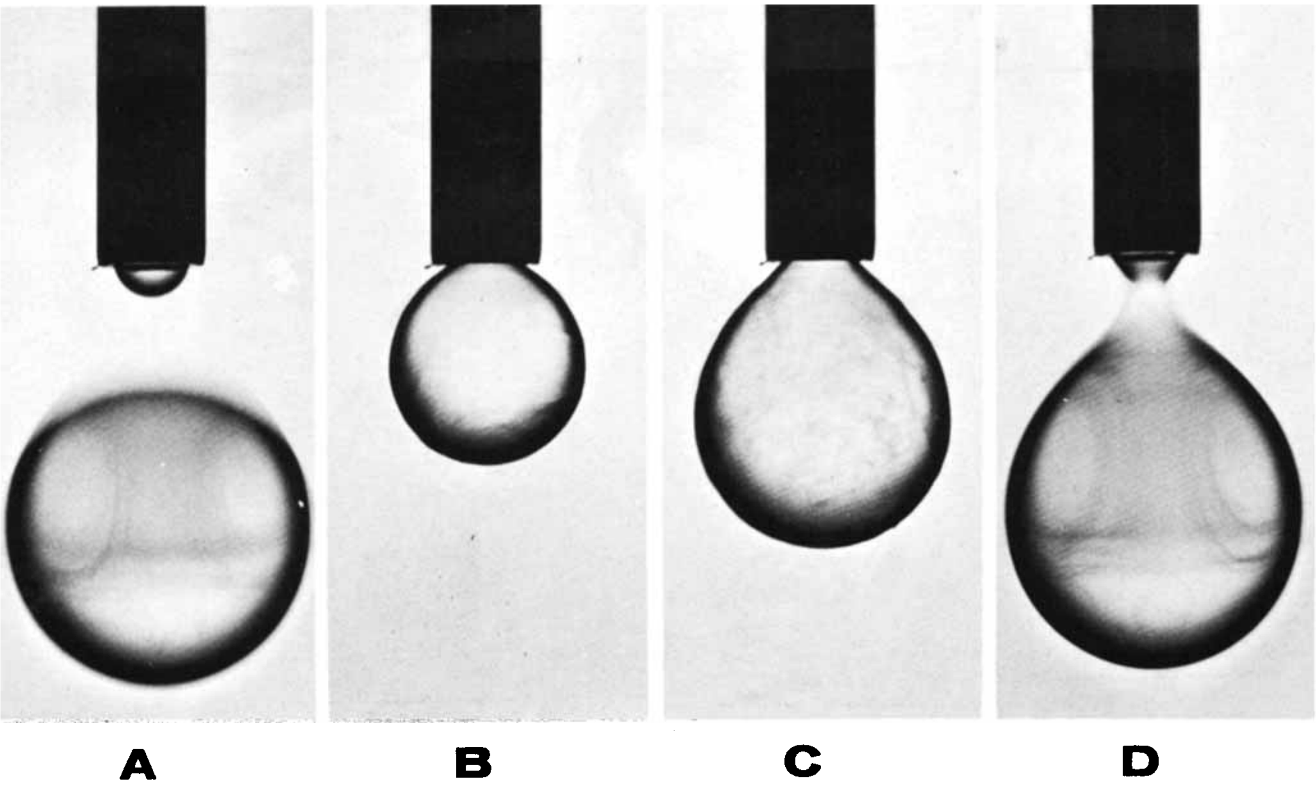

Fig. 4. Drop formation lifetime. *A*, initial condition; *B*, early in formation period; *C*, late in formation period; *D*, terminal condition.

eight drops were formed in succession. A drop formed near the middle of this series was selected from the film for analysis.

The mass transfer during formation was determined by analyzing for total drop volume at least 25 different frames from one drop formation sequence. This provided the actual volume of that drop at 25 different times approximately equally spaced between the initial drop and its termination at break-off. Figure 4 shows typical initial and final conditions with two intermediate points. Each such drop photograph was evaluated by assuming the drop to be axisymmetric with respect to the nozzle axis. The drop axis was divided into 30 increments, regardless of its length, and the drop diameter was measured at the beginning and end of each increment. Each division was approximated as the frustum of a cone in a computer program which evaluated both the volume and the surface area of the drop. A measure of the nozzle diameter was used to obtain the optical magnification factor.

Since the dispersed phase feed rate was known, the total mass transfer up to any time could be evaluated from the measured volume at that time. The computer program (*11*) then determined mass transfer and surface area for each time recorded and fit these two functions to third-order polynomials (neglecting any data points outside three standard deviations). From this smoothed data, mass transfer rates and coefficients were calculated as a function of time during formation.

Errors

Since the technique developed here requires the evaluation of small differences between large numbers, an estimate of the maximum errors to be expected is included to aid the reader in evaluating the results. A typical drop segment, represented as a frustum of a cone, might have diameters of 1.0 and 1.1 in. and length of 0.06 in. on the film analyzer screen. The measuring cross hairs could be positioned to within 0.001 in.; thus the maximum error in any length measurement should be 0.002 in. Thus the maximum error in surface area would be 1.7% and in volume 0.4%. Since the total mass transfer ranged from 1.4 to 26% of the final drop volume, such errors could be significant at the lower transfer rates. However, since the drop volume was evaluated at least 25 times in each formation and these values fit to a smooth curve, random measurement errors should be held to a minimum. The smoothness of the data with the computer fit equation is taken as evidence of very good reproducibility of measurement; mass transfer numbers were on the order of 10^{-3} g. and the standard deviation of the fit curves on the order of 10^{-5} g. Any data point further from the curve than three standard deviations was rejected and this rarely involved more than two points and often none.

It is not possible to detect any transfer of water into the droplet, so great care was exercised to be certain that the dispersed phase was completely saturated with water prior to a run. An additional uncertainty would be introduced by a large heat of solution. However, for this system it is small and heat dissipation is rapid because of the high ratio of Schmidt to Prandtl numbers (~ 100). The possibility of an accumulation of impurities during the course of this investigation is considered unlikely because of the good reproducibility of results observed in several duplicate runs made at the beginning and end of experimentation and because of the lack of surfactant materials even in our untreated laboratory water as evidenced by interfacial tension measurements.

RESULTS AND DISCUSSION

The operating parameters covered in this study are listed in Table 2. A condensed summary of the mass transfer results obtained is presented in Table 3, for which integrated average coefficients for the total formation period have been been evaluated. In order that specific effects might be more readily seen, a graphical presentation of instantaneous mass transfer coefficients is also made. In Figures 5 through 8 the variation of the coefficient with time during formation is shown with various formation characteristics as parameters. In every case the coefficient is initially very large but rapidly falls; in most cases it then remains nearly constant at the lower level, although in a few instances it appears to rise again. The implication of this behavior is that convection generated in the drop by the velocity of the fluid leaving the nozzle exerts a significant influence on the mass transfer. The importance of such convection may be assumed to be greatest when the drop size is smallest. Since this system is taken to be continuous phase resistance controlled, the effect would have to be transmitted across the interface to influence the boundary layer around the drop. However, this assumption appears to be justified by the parametric effect of dispersed phase velocity shown for a fixed nozzle cross section in Figure 5 and for a fixed volumetric flow in Figure 6. In both cases the mass transfer coefficient is seen to increase with increasing velocity from the nozzle.

The same pattern as shown in Figure 5 was observed for the larger diameter nozzles, but the effects were not so pronounced. The large difference between the mass transfer coefficients for the smaller two nozzles and the coefficient for the largest nozzle, evident in Figure 6, is taken as evidence of little internal convection in the latter case. A comparison of the average coefficient for this largest nozzle to those reported for slow formation and transfer controlled by diffusion in the continuous phase (*10*) shows good agreement. Since the inflow velocity is the lowest and the overall drop size the greatest for this nozzle, the lack of any substantial effect is not too surprising.

Figure 7 shows the effect of the continuous phase flow rate on the mass transfer behavior. Although the coefficient increases with increasing Reynolds number, the effect is small. It appears that the dispersed phase flow rate is at least as important as that of the continuous phase in determining the mass transfer rate. However, the exponent in the dependence of total mass transfer on time increases with increasing continuous phase Reynolds number (see Table 3).

TABLE 2. OPERATING PARAMETERS

Nozzle:	Gauge No.	O.D., in.	I.D., in.
	16	0.065	0.047
	18	0.049	0.033
	20	0.035	0.023

Dispersed phase feed rate: 0.396 to 1.584 cc./min.
Continuous phase flow rate: 2.7 to 11.1 cc./min.
Continuous phase Reynolds number: 15.7 to 64.7

The effect of adding surface-active agent, 45 p.p.m. Triton X-100, to the continuous phase is indicated in Figure 8. The fact that small effects in opposite directions are observed for two different nozzle sizes is taken as evidence that there are no strong effects of interfacial tension driven instabilities on the measured mass transfer rates. The ra-

TABLE 3. CHARACTERISTIC RESULTS FROM ALL RUNS

	Formation conditions†	Formation time, sec.	Total mass transfer, g. × 10^4	Time average mass transfer coefficient, cm./sec.	n, slope*
20 g.	1.5839 cc./min.	0.629	43.57	1.081	0.578
	1.3723 cc./min.	1.065	41.17	0.169	1.020
	0.7953 cc./min.	1.548	29.18	0.110	0.907
	0.3960 cc./min.	3.145	30.55	0.048	0.983
18 g.	1.5839 cc./min.	1.081	34.68	0.150	0.956
	0.7953 cc./min.	2.242	38.85	0.074	0.865
	0.3960 cc./min.	4.339	42.02	0.043	0.927
16 g.	1.5839 cc./min.	1.726	6.79	0.012	0.710
	0.7953 cc./min.	3.097	17.82	0.012	1.453
	0.7953 cc./min.	3.339	7.99	0.007	1.333
	0.3960 cc./min.	5.790	13.78	0.006	1.714
	0.3960 cc./min.	6.048	19.77	0.007	2.376
18 g.	$N_{Re} = 15.7$	2.403	40.75	0.072	0.899
	$N_{Re} = 31.5$	2.387	40.38	0.065	0.922
	$N_{Re} = 64.7$	2.274	47.54	0.079	1.036
18 g.	SAA	2.875	45.08	0.051	0.940
16 g.	SAA	5.610	28.51	0.013	1.301

†Continuous phase Reynolds number is 15.7 except as noted.
*Cumulative mass transfer = const. (formation time)^n

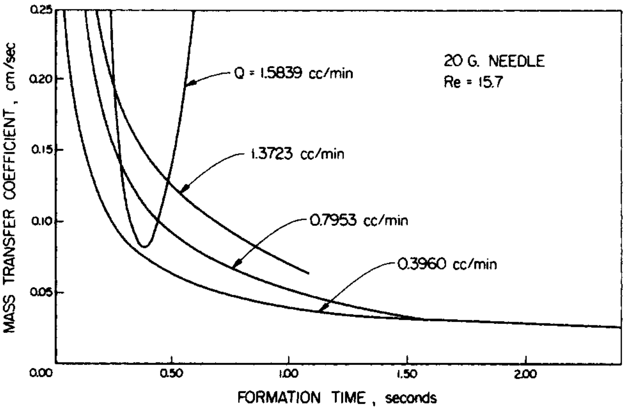

Fig. 5. Effect of dispersed phase velocity on mass transfer coefficient during drop formation, smallest nozzle.

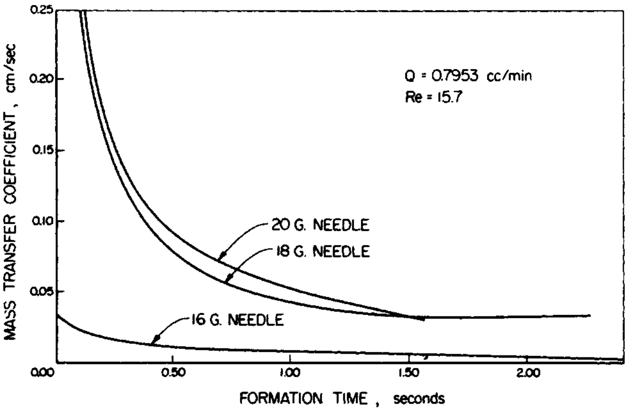

Fig. 6. Effect of nozzle diameter on mass transfer coefficient during drop formation.

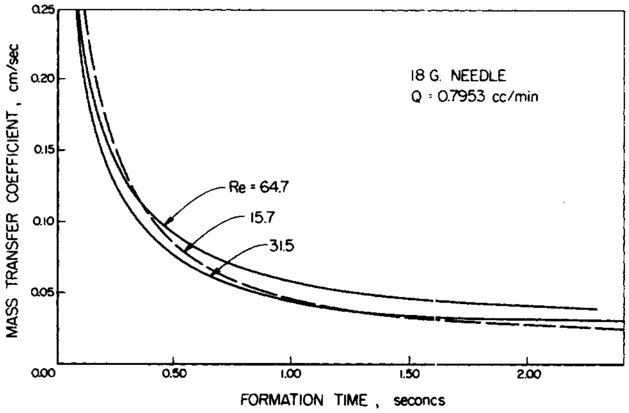

Fig. 7. Effect of continuous phase flow rate on mass transfer coefficient during drop formation.

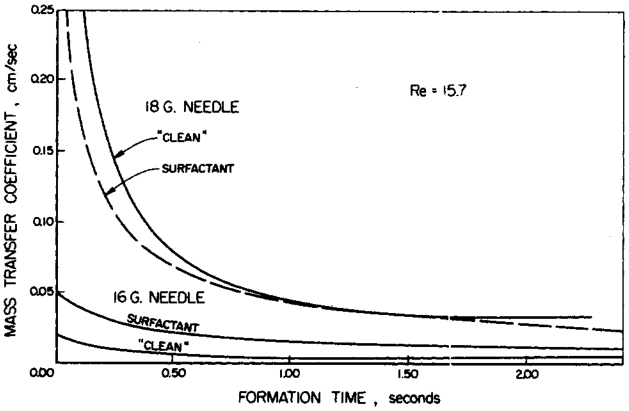

Fig. 8. Effect of surface-active agent on mass transfer coefficient during drop formation.

Table 4. Comparison of Total Mass Transfer

	Formation transfer, g. × 10^4		
	20 gauge	18 gauge	16 gauge
Surface stretch model	3.09	4.83	8.36
Fresh surface elements	3.59	5.60	9.70
Experimental results	29.18	38.85	7.99

tionalization applied to the observed effects is the following: for the smaller nozzle where internal convection has been judged to be important, the presence of a surfactant film may be assumed to reduce the mobility of the interface and thus lower its ability to transmit shear to the continuous phase. This would reduce any increase in mass transfer caused by the internal flow, especially at early times when the drop is small and this effect largest. For the largest nozzle, however, no effect of internal flow had been found in the absence of surfactant; therefore no reduction should be expected. The small increase in mass transfer in the presence of surfactant may be attributed to an increase in surface deformation in the form of waves which were observed only for formations on the large nozzle and which increased noticeably when surfactant was added.

The total mass transferred during formation has been calculated for the surface stretch and the fresh surface elements models and is compared with experimental results in Table 4. No specific comparisons have been made to the work of Angelo et al. (*1*) since these authors have shown that, for drop formation, their prediction is lower than that of the fresh surface elements model as should be expected of a more general form of the surface stretch model. As already noted, only the results with the largest nozzle compare well with the predictions. The more rapid transfer for the other cases has been assumed to be caused by convection resulting from the rapid inflow of material to the drop. This mass transfer system exhibits a high Schmidt number (1,000) so that any convection induced near the interface would be expected to influence the mass transfer rate strongly. The implication of the results obtained is that convection caused by the dispersed phase flow is more important than continuous phase convection. It is probably important at this point to note that the nozzle velocities in this study ranged from 0.6 to 9.9 cm./sec., where those employed by Popovich et al. were from 0.07 to 1.1 cm./sec.

Equation (3) has been assumed for the variation of surface area with formation time in both the surface stretch and the fresh surface models. Figure 9 indicates that a typical surface area variation is well represented in this way after a brief initial period. However the above models then require an equation of the form

$$\text{mass transfer} = \text{const} \times t^{0.5} \tag{4}$$

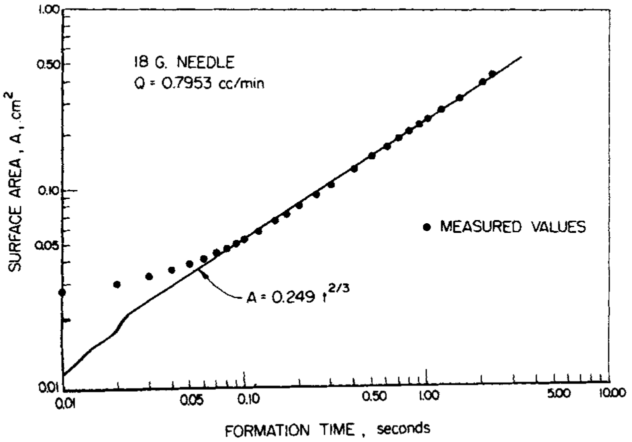

Fig. 9. Interfacial area of a forming drop.

It is obvious from the exponents given in Table 3 that a square root dependence on time will not describe the measured transfer. The least squares exponent is always greater than 0.5 and generally greater than 0.9. This may be taken as further evidence that unsteady state diffusion alone is insufficient to describe the mass transfer occurring during drop formation.

As a final comparison, the mass transfer coefficient expected for continuous phase resistance only was calculated for a free drop falling at its terminal velocity to be 0.003 cm./sec. (*3*). The time average coefficients reported here for formation are an order of magnitude greater for the smaller nozzles, and even for the largest nozzle exceed this value by a factor of 3 to 4. With such rapid initial transfer, the formation period could represent a significant fraction of the total mass transfer in a contactor.

CONCLUSIONS

A technique for the direct measurement of mass transfer during drop formation has been developed and applied to the rapid formation of slightly soluble organic drops in water. The strong effect of convection during formation has been demonstrated for this high Schmidt number system. The observed mass transfer coefficients are largest in the initial stages of formation when convection is most significant but even the average for the entire formation period is substantially greater than for a free drop.

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NOTATION

A = interfacial area of drop, sq. cm.
C = concentration of transferring species, g./cc.
d = diameter of drop, cm.
D = diffusivity, sq. cm./sec.
k = constant in Equation (2)
n = exponential term in time-dependent relations
N_A = interfacial mass flux, g./(sq. cm.)(sec.)
t = time from beginning of formation, sec.

Subscripts

f = condition at end of formation period
o = initial value
s = saturation value

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