Surface Phenomena and Mass Transfer Interactions in Liquid-Liquid Systems

Part I: Droplet Formation at a Nozzle

The surface dynamics of pendant aqueous droplets forming at a submerged nozzle in an immiscible organic solvent have been studied using a novel laser-activated photochromic tracer technique. This enabled a small element of surface to be labeled so that its subsequent history could be recorded photographically.

Results for aqueous droplets forming in toluene in the absence of any mass transfer indicated only a slow interfacial circulation from the front to the rear, and there was no indication of any surface renewal as a result of hydrodynamic flow even at nozzle Reynolds numbers as high as 300. By contrast, the introduction of any one of a number of organic solutes into the toluene phase led to sporadic Marangoni-type interfacial disturbances, which in turn resulted in rapid replacement of elements of the droplet surface. It is proposed that renewal of the droplet surface is dependent on solute diffusion in the present instance and that the processes of surface renewal and mass transfer are likely to be interactive.

J. D. THORNTON
T. J. ANDERSON
K. H. JAVED
and S. K. ACHWAL

Department of Chemical Engineering,
The University, Newcastle upon Tyne,
NE1 7RU, England

SCOPE

Mass transfer rates in liquid extraction systems are generally interpreted in terms of the well-known film theory due to Lewis (1916) and Lewis and Whitman (1924). Thus solute transfer is imagined to proceed by steady-state molecular diffusion through thin laminar layers on either side of the interface, and the effect of hydrodynamics is confined to an influence on the thickness of these laminar films. There are, however, a number of alternative theories that consider particularly the second of these assumptions, and all have in common that they postulate an exchange of fluid between the interface and the bulk phases. Thus the theory due to Highbie (1935), when applied to a moving droplet, argues that fresh surface is continuously created in the region of the front stagnation point and convected to the rear by virtue of the no-slip condition with the continuous phase. There is therefore a regular replacement of the surface layers by bulk fluid, and mass transfer proceeds by diffusion in the intervals. However, because of the surface renewal, this transfer is a transient rather than a steady-state process. More recently, Danckwerts (1951, 1955) has proposed a surface renewal mechanism based on the random intrusion of turbulent eddies into the interface with, once again, transfer proceeding by transient molecular diffusion between successive disturbances. Another contribution, due to Kishinevski and Pamfilov (1949), also argues in favor of turbulent renewal but differs from the other theories in that these authors suggest that turbulent convection may be the dominant mechanism of solute transfer. The one aspect common to all three renewal theories is that the surface replacement mechanism is directly linked to the system hydrodynamics.

Past attempts to differentiate between these theories have relied almost exclusively on indirect evidence obtained from mass transfer experiments and have generally been inconclusive. The one exception is the gas-liquid interface in a well-stirred cell, for which Davies and Khan (1965) demonstrated surface renewal by turbulent eddies by following the motion of talc particles spread on the surface. It is doubtful, however, whether the high levels of turbulence present in a stirred cell would be relevant to droplet systems. On the other hand, direct observation of the behavior of droplet surfaces using talc particles would be difficult and a new experimental approach is required.

The present work was therefore undertaken in order to develop a method for observing directly the behavior of the droplet interface in liquid-liquid systems and in particular the interfacial characteristics of pendant aqueous droplets forming in an

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T. J. Anderson is currently at the Melbourne and Metropolitan Board of Works, Melbourne, Australia. K. H. Javed is currently at the Department of Chemical Engineering, University of Engineering and Technology, Lahore 31, Pakistan. S. K. Achwal is currently at the Department of Chemical Engineering, University of Petroleum and Minerals, Dhahran, Saudi Arabia.

Correspondence concerning this paper should be directed to J. D. Thornton at Lochhouse Tower, Moffat, Dumfriesshire DG10 9SF, Scotland.

immiscible organic phase. This situation is of relevance to the design of liquid extraction columns, since an appreciable fraction of the total mass transfer achieved in such devices is known to occur during the droplet formation period at the distributor. The technique relies upon a finely focused ultraviolet laser pulse to induce a local color change in a suitable photochromic tracer dissolved in the dispersed phase, thereby labeling a small element of the droplet surface. The subsequent behavior of this spot is then recorded by high-speed photography. The use of photochromic tracers has been described previously by Hummel and coworkers (Popovich and Hummel, 1967, Humphrey et al., 1974a), but they apparently failed to find a tracer suitable for use in the region of liquid-liquid interfaces (Humphrey et al., 1974b). This difficulty was overcome in the present work by using the photochemical reduction of potassium ferric oxalate in aqueous media as a color tracer (Calvert and Pitts, 1964). The paper elaborates and extends the findings briefly reported earlier by Thornton and Anderson (1981).

CONCLUSIONS AND SIGNIFICANCE

The most significant feature of the experiments conducted in the absence of mass transfer was the complete lack of any surface renewal as a result of hydrodynamic flow. This observation was true of both forming droplets, even at nozzle velocities bordering on the jetting regime, and of a limited number of observations of freely falling droplets. In both cases, however, a slow recirculation of the surface was observed that was consistent with the arguments advanced by Highbie (1935).

By contrast, observations of the interface in the presence of an undistributed solute showed a series of rapid Marangoni-type disturbances, which in turn gave rise to local renewal of the droplet surface. It therefore appears likely that Marangoni-induced surface renewal is the mechanism by which mass transfer rates in liquid-liquid systems are increased beyond those expected for molecular diffusion alone. This contention is supported qualitatively by a number of authors (e.g., Sawistowski and Goltz, 1963), but the present technique does have the advantage that a quantitative analysis becomes possible.

The fact that, in the present instance, surface renewal was observed only in the presence of mass transfer also implies that the two processes are likely to be interactive. If subsequent work proves this to be a general rule, it could have important implications for the modeling of liquid extraction processes as a whole.

EXPERIMENTAL

The aqueous dispersed phase containing the chemical tracer was a pale yellow-green color prior to irradiation by the laser. It was made up freshly as required and was composed of the three constituent solutions described in Table 1, mixed in the ratio 2:2:1. Irradiation of this mixture by light of the appropriate wavelength results in the simultaneous reduction of ferric ions and oxidation of oxalic acid. The ferrous ions so produced are detected by the formation of an intense blue suspension of ferrous ferricyanide, and the sodium acetate solution is provided as a buffer. A similar tracer has been used by Goldish et al. (1965) to measure axial dispersion in laminar pipe flow, but it was apparently dismissed by Hummel and coworkers since the color was slow to develop (Popovich and Hummel, 1967). However, the present tracer, which differs chemically from that used by Goldish et al., develops in less than 4 ms and has proved adequate for the present application.

Subdued incandescent light does not substantially affect the solution color, since the reaction is primarily sensitive to blue and ultraviolet wavelengths (Calvert and Pitts, 1964). The color change upon irradiation corresponds to strong absorption beyond 600 nm and can be accentuated by the use of a suitable optical filter.

TABLE 1. TRACER COMPONENTS*

Solution	Composition
A	18.4 g potassium ferric oxalate $K_3Fe(C_2O_4)_3.3H_2O$ 25 mL 1N H_2SO_4 Distilled water to make up volume to 250 mL
B	13.4 g potassium ferricyanide, $K_3Fe(CN)_6$ Distilled water to make up volume to 250 mL
C	12.3 g sodium acetate, $NaCH_3COO$ 80 ml 1N H_2SO_4 Distilled water to make up volume to 250 mL

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* Mixed in 2:2:1 ratio.

Throughout the work, steps were taken to avoid contact between metallic surfaces and the tracer solution, since the latter produced a colored solution when in contact with common metals. The tracer solution had a specific gravity of 1.059 and a viscosity about 4.6% greater than water over the range 20 to 25°C.

The basic experimental arrangement was determined by the need to disperse the aqueous phase in view of the fact that the tracer was only water-soluble. This had the result that the refractive index of the droplet would almost always be less than that of any continuous organic phase. It was therefore necessary for the laser beam to strike the droplet at an angle approaching 90° to prevent total internal reflection, and the subsequent behavior of the labeled interface had to be viewed along the axis of the laser.

A schematic diagram of the resultant experimental arrangement is shown

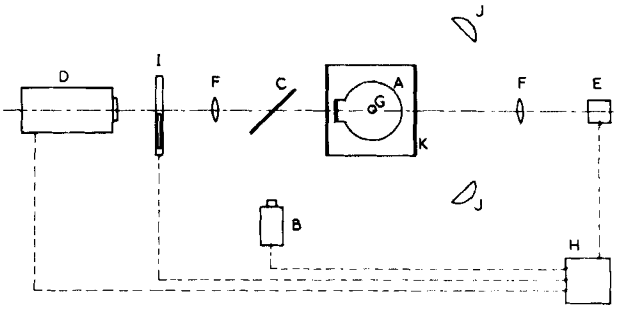

Figure 1. Experimental arrangement.

A = test cell.
B = cine camera.
C = mirror.
D = pulsed ruby laser.
E = photocell.
F = quartz lenses.
G = glass nozzle.
H = control box.
I = optical filter.
J = photoflood lamps.
K = thermostatted tank.

in Figure 1. The cylindrical borosilicate glass test cell (*A*) was 8 cm in diameter, 15 cm high, and fitted with a planar window to provide an undistorted view into the cell as well as a point of entry for the ultraviolet laser pulse. Borosilicate glass was chosen in view of its low absorbtion at the laser wavelength (347 nm). The test cell was viewed by a 16 mm Bolex cine camera (*B*) through the planar mirror (*C*), mounted at 45° to the laser beam and equipped with a small hole to allow transmission of the light pulse. The pulsed ruby laser (*D*) provided output at two wavelengths (200 mJ at 694 nm and 50 mJ at 347 nm in 30 ns) and included a colinear 2 mW continuous He-Ne laser that irradiated the photocell (*E*) via two quartz focusing lenses (*F*). A droplet forming at the glass nozzle (*G*) obscured the beam to the photocell and activated the control box (*H*). This device had a number of functions. It immediately started camera (*B*) and switched the filter (*I*) into the beam path. This filter was chosen to exclude the He-Ne wavelength (633 nm) and, more importantly, to exclude the ruby laser output at 694 nm while allowing transmission of the ultraviolet energy at 347 nm. The control box also triggered the ruby laser after a variable delay, suitably chosen to allow the camera to reach full running speed and the filter to be switched into the light path. Finally, the control box stopped the camera after a suitable running period. Illumination was provided by photoflood lamps (*J*) mounted to allow viewing of the pendant droplets by transmitted light, and the camera lens was fitted with an optical filter to accentuate the green to blue color transition in the droplet surface. The test cell was enclosed in a constant temperature bath in order to eliminate all thermal convection currents.

This arrangement allowed a small element of surface (≈ 1 mm^2) of a forming droplet to be labeled in a wide range of positions by varying the location of nozzle G relative to the fixed axis of the He-Ne laser beam and by varying the control box delay before the pulsed laser was activated.

EXPERIMENTAL RESULTS

Tracer Tests

The organic spiropyran dye, 1,3,3-trimethylindolino-6′-nitrobenzospiropyran (TNBSP), used by Hummel and coworkers, suffered from the disadvantage that an induced local color change at a liquid-liquid interface was invariably accompanied by a disturbance. This disturbance was particularly severe in the case of an equilibrated, stationary pendant drop and took the form of an initial eruption toward the light source (Humphrey, 1974b). Similar disturbances were observed by the present workers who used this dye prior to adopting the inorganic tracer, and the effect has been attributed to a decrease in interfacial tension. The explanation appears to lie in the work of Van Voorhis et al. (1970), who measured the interfacial tension between water and toluene containing 10^{-3} M of TNBSP and found a decrease of up to 10% on exposure to ultraviolet light. The effect in the case of Hummel's experiment, where the concentration of TNBSP was about 0.5×10^{-3} M, could be expected to be similar, although the organic phase was chlorobenzene in this case. Thus there was a decrease in the interfacial tension in the region labeled by Hummel's laser and fluid within the droplet, which is at a higher pressure than fluid outside, erupted through the affected region.

The present tracer system does not suffer from this disadvantage. A sequence of photographs at 20 ms intervals of a stationary equilibrated droplet in toluene before and after exposure to the ultraviolet laser confirmed that there was no immediate disturbance on irradiation nor any subsequent disturbance following the appearance of the colored tracer spot on the droplet surface.

On some occasions and with some batches of tracer solution, however, a symmetric expansion of the colored region occurred immediately after the laser triggered. This effect was not reproducible, nor did it ever cause a macroscopic disturbance to the drop or appear to induce any convection in the interface. It could not be traced to the chemical constituents of the tracer, the distilled water used in its preparation, or the age of the solution and was probably caused by a very small decrease in interfacial tension. The importance of the phenomenon is discussed later.

The time sequence photographs referred to above can be regarded as an indication that the static surface properties of the aqueous tracer solution are not altered by exposure to ultraviolet light when the second phase is toluene. An additional check was also made to ensure that the dynamic behavior of the interface was also insensitive to ultraviolet light. This test was based on the surface viscosity of the solution, which was measured by a rotational viscometer of the type described by Kanner and Glass (1969). There

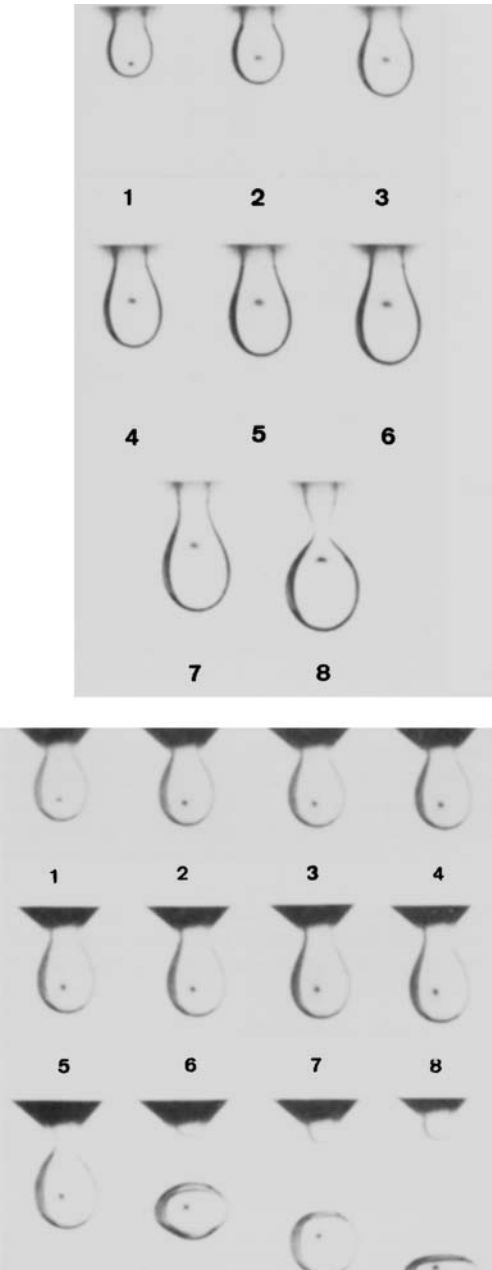

Figure 2. Growing pendant droplets in toluene without mass transfer.

Re_N: 169. D_N: 0.331 cm.
v_N: 4.85 cm/s. Frame interval: 50 ms.
(a) During formation. (b) Formation and detachment.

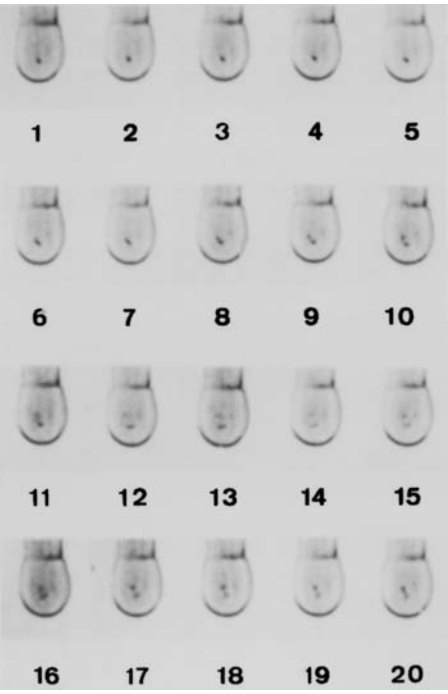

Figure 3. Growing pendant droplet in toluene containing 3 v/v% diacetone alcohol.

Re_N: 42. D_N: 0.417 cm.
v_N: 0.920 cm/s. Frame interval: 4 ms.

was no detectable difference between the behavior of the exposed and parent dye solutions. Unfortunately, the sensitivity of the instrument, which Kanner lists as 10^{-3} surface poise, was such that the Newtonian behavior of the interface could not be verified.

Finally, the depth of penetration of the laser pulse was estimated by viewing droplets in a direction normal to the beam. The depth of penetration was relatively small at high tracer concentrations, and therefore a series of penetration measurements was carried out over a range of dilutions. The data, when plotted in the form log penetration vs. log concentration, had the expected slope of -1, and extrapolation to the working tracer concentration indicated a depth of penetration of approximately 50 nm.

A similar result was obtained from measurements of the extinction coefficient of diluted solutions at the laser wavelength.

Surface Dynamics of Growing Droplets in the Absence of Mass Transfer

A typical sequence of photographs for an equilibrated aqueous droplet growing in toluene is shown in Figures 2a and 2b. There is no indication of any disturbance to the tracer spot either during formation (Figure 2a) or after detachment (Figure 2b), and this observation was verified for nozzle Reynolds numbers, Re_N, as high as 300. Much the same conclusions have been formed from a limited number of films of freely falling droplets, some of which oscillated markedly and presumably were turbulent. The results indicate that surface renewal due to hydrodynamic turbulence as proposed by Danckwerts (1951) does not occur in equilibrated droplet systems.

The results do provide evidence, however, that the surface circulates toward the rear of the droplet. An indication of this effect can be formed by measuring the vertical distance between the spot and the drop apex. This dimension increased with time for all the droplets studied over a wide range of nozzle Reynolds numbers ($42 \leqslant Re_N \leqslant 300$), irrespective of whether the droplet was initially labeled near the apex, near the major diameter, or approximately midway between the major diameter and the nozzle. These results spanned the latter 70% of the drop formation period.

This trend is consistent with published work using suspended tracers in the dispersed phase, which generally indicates that recirculation of the droplet interior commences in the range $10 \leqslant Re_N \leqslant 35$ (Burkhart et al., 1976). Thus the recirculation of the surface noted here for Reynolds numbers beyond 42 is not unexpected.

Surface Renewal of Growing Droplets with Mass Transfer

Cine films obtained with an undistributed solute in the organic phase were striking in that the laser-induced spot experienced a series of violent, sporadic disturbances of which the sequence shown in Figure 3 is typical of the appearance of the spot after a single disturbance. Furthermore, these disruptions persisted for a measurable period of time, although this interval was difficult to determine since the disturbances tended to decay slowly. The start of a disturbance was, however, generally sudden and readily identifiable. This behavior was verified for a number of solutes (3 v/v% diacetone alcohol, 2 v/v% propionic acid, and 4 v/v% acetone) transferring from the continuous toluene phase to the aqueous droplet and also for the two-component system, aqueous tracer solution/ethyl acetate. This effect was qualitatively independent of nozzle Reynolds number and was apparent even at zero nozzle flow rates until the droplet had reached equilibrium.

In view of the results obtained in the absence of mass transfer, this phenomenon must be due to the presence of unequilibrated solute. Interfacial disturbances of this type are loosely classed as Marangoni effects, and a basic theoretical description, due to Sternling and Scriven (1959), argues that the phenomenon is due to spatial variations in interfacial solute concentration that arise spontaneously during mass transfer. Under favorable conditions, the consequent interfacial tension gradients induce a flow in the plane of the interface that must be supplied by fresh fluid from the bulk. Thus Sternling and Scriven argue that the phases near the interface consist of a number of "roll cells." These cells have been detected by Schlieren photography in a direction normal to both planar and droplet interfaces and, in addition, the basic flow patterns have been verified by tracer photographs parallel to a planar interface (Sawistowski, 1971). The present observations are in line with Sternling and Scriven's criterion for surface turbulence, inasmuch as the concentration coefficient of interfacial tension for the system was negative and instability coincided with solute transfer out of the phase of lower diffusivity.

The experimental runs were divided into three basic groups according to whether the droplet was initially labeled near the apex, the major diameter, or the nozzle. In all cases the laser was triggered when the droplet had reached about 30% of its final volume; the continuous phase was toluene containing 3 v/v% diacetone alcohol.

Two sets of measurements were derived from the cine film for each of the three positions:

1. The time interval between the creation of the laser spot and the onset of the first disturbance.
2. The time intervals between the commencement of successive disturbances after the first (i.e., subsequent disturbances).

Normally about three disturbances were observed before the tracer spot was dissipated or the drop detached from the nozzle.

For the purposes of this work, a disturbance was defined as a sudden alteration in the shape or position of the tracer spot with a clear, identifiable commencement. Thus there was the possibility that consecutive disturbances very close together were not detected, since the onset of the second eruption would not be readily iden-

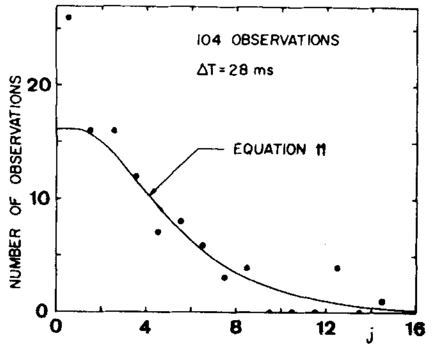

Figure 4. Histogram of first disturbances for the region near the major diameter.

Plot of Eq. 11 shown for comparison using $\hat{t}$ value in Table 2; ΔT = 28 ms.

tifiable until the first had partly dissipated. In addition, the film speed (250 frames/s for all mass transfer measurements) limited the resolution with which the commencement of a disturbance could be detected to 4 ms.

Every labeled spot was observed to experience a first disturbance. Unfortunately, on a few occasions, the time interval before the onset of the second disturbance was so long that the droplet detached, thereby terminating the experiment. This problem, which represents a "censoring" of the measurements because long intervals are excluded, became increasingly severe for disturbances subsequent to the second.

Results from all three regions of the droplet surface were similar to the frequency histograms of first, second, and third disturbances for drops initially labeled near the major diameter shown in Figures 4, 5, and 6, respectively. The most important features of these figures occur in the histograms of subsequent disturbances. Thus, for the region near the major diameter, Figures 5 and 6 indicate that no disturbances were ever observed within 28 ms of the onset of a previous disturbance. The corresponding time intervals for the regions near the nozzle and the apex were 40 ms and 12 ms, respectively. Thus, for any point on the droplet surface, the time interval between the onset of successive disturbances may be regarded as the minimum duration (A) of a perturbation.

A second feature of the figures is that the curves generally rose to a maximum before falling toward zero. The implications of this observation that the most likely residence time at the surface is finite are discussed in the next section. Finally, since the disturbances did not decay instantaneously, the laser should have labeled existing perturbations on occasions. This proved to be the case, and immediate disturbances were noted in some instances as soon as the laser was triggered.

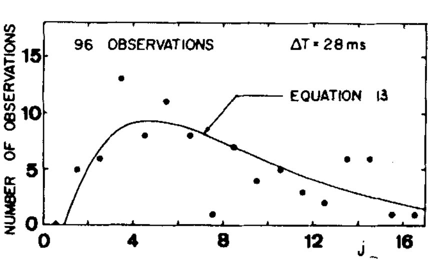

Figure 5. Histogram of second disturbances for the region near the major diameter.

Plot of Eq. 13 shown for comparison using $\hat{t}$ value in Table 2; ΔT = 28 ms.

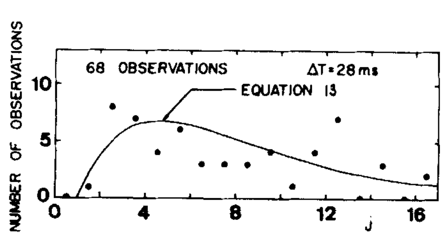

Figure 6. Histogram of third disturbances for the region near the major diameter.

Plot of Eq. 13 shown for comparison using $\hat{t}$ value in Table 2; ΔT = 28 ms.

INTERPRETATION OF RESULTS

One of the most striking features of the present work is the complete absence of surface renewal in the absence of mass transfer. This is particularly surprising in view of the well-known circulation patterns inside forming droplets. All the data indicate a complete absence of surface mixing due to turbulent eddies at the interface and thus imply that there is no perpendicular component of velocity at the droplet surface. Whether this is a generalized phenomenon remains to be established; it should be noted, however, that while the present water/toluene system has viscosities and densities in the normal range for liquid-liquid systems, the interfacial tension is relatively high at 34 dyne/cm. It would therefore be pertinent to examine the surface behavior of other aqueous/organic solvent systems of lower interfacial tension before regarding the present findings as being of general applicability.

The situation in the presence of mass transfer is totally different, and renewal of fluid in the droplet surface is seen to come about through the agency of interfacial disturbances that accompany the transfer process. The droplet surface may therefore be thought to comprise a large number of microelements, each of which may be subjected to a disturbance. If it is further assumed that there are no stagnant zones within the surface, then the arrival of a disturbance at any particular moment may be regarded as terminating the life of that element.

The nature of interfacial disturbances may take several forms, depending on the characteristics of the extraction system and the time of exposure of the interface; the current position has been well summarized by Sawistowski (1971). During the present work, no gross disturbances or perturbations of the droplet profile were observed, and it is therefore not unreasonable to suppose that interfacial disturbances were largely due to the formation of convection or roll cells so that the duration of a disturbance may thus be equated to the lifetime of the associated roll cell.

The present set of measurements relate to two basic quantities; those relating to the first disturbances determine the life expectation of the fluid elements already in the surface from the time when the laser was triggered up to the time of the first disturbance. Since the life expectation frequency function is equal to the age frequency function (Zwietering, 1959), measurement of life expectations as determined by the occurrence of first disturbances will yield the age frequency function $\phi(\theta)$. On the other hand, each of the subsequent disturbances is an indication of the residence times of the fluid elements, since it measures the total life of an element between successive disturbances. The measurement of these time intervals therefore determines the cumulative residence time distribution $F(t)$. The relationships between these quantities and the residence time frequency function $f(t)$ are well known (Zwietering, 1959; Koppel et al., 1966) and take the form

$$\phi(\theta) = \frac{1}{T_*}[1 - F(\theta)] \qquad (1)$$

where the mean residence time T^* is given by

$$T^* = \int_0^\infty t dF \tag{2}$$

and the residence time frequency function by

$$f(t) = \frac{dF(t)}{dt} \tag{3}$$

The implications of these relationships for surface renewal models have been discussed by Perlmutter (1961). Thus, for example, the well-known Dankwerts expression for the age frequency function written in terms of τ rather than its reciprocal s becomes

$$\phi(\theta) = \frac{1}{\tau} \exp(-\theta/\tau) \tag{4}$$

and corresponds to a residence time frequency function of identical form. This expression is based on the assumption that $\phi(\theta)$ is governed by a single random event (i.e., the arrival of a disturbance is the sole prerequisite for surface renewal and has a probability independent of time) and, unlike the results shown in Figures 5 and 6, has the consequence that the most likely surface residence time is zero.

The observations in this work, however, suggest that the residence time frequency function of the surface may well be determined by two contributions: (1) the duration of a roll cell and (2) the probability that an undisturbed surface element becomes disturbed.

It seems likely that the duration of a roll cell is a variable parameter, particularly in view of Figure 3, which shows a roll cell of about 40 ms duration under the same conditions as Figures 5 and 6, which indicate a minimum duration (A) of about 28 ms. Thus, if it is assumed that roll cells have a minimum duration A and then terminate with a probability independent of time and determined only by the time constant τ_d, the residence time frequency function for a disturbance $f_d(t)$ is given by

$$f_d(t) = \begin{cases} 0 & 0 \leqslant t \leqslant A \\ \dfrac{1}{\tau_d} \exp(-t'/\tau_d) & 0 < t' < \infty \end{cases} \tag{5}$$

where $t' = (t - A)$.

If a second process with time constant τ_i is also assumed for the interval between disturbances, the corresponding residence time frequency function may be represented by

$$f_i(t) = \frac{1}{\tau_i} \exp(-t/\tau_i) \tag{6}$$

The frequency density function for the two processes in series can be calculated from the well-known result

$$f(t) \int_0^t f_i(t-u) f_d(u) du \tag{7}$$

If it is further assumed that $\tau_i = \tau_d = \tau/2$ (where τ is the total time constant), the final expression for $f(t)$ is

$$f(t) = \begin{cases} 0 & 0 \leqslant t \leqslant A \\ \dfrac{4t'}{\tau^2} \exp(-2t'/\tau) & A < t < \infty \end{cases} \tag{8}$$

This expression is similar to Eq. 20 proposed by Perlmutter (1961) to overcome the deficiencies noted earlier in Eq. 4 except for the inclusion of A, which is equivalent to a "dead time effect."

The age frequency function equivalent to Eq. 8 can be found from Eqs. 3, 2, and 1:

$$\phi(\theta) = \begin{cases} 1/(\tau + A) & 0 \leqslant \theta \leqslant A \\ \dfrac{1}{\tau + A}\left(1 + \dfrac{2\theta'}{\tau}\right) \exp\left(-\dfrac{2\theta'}{\tau}\right) & 0 < \theta' < \infty \end{cases} \tag{9}$$

where $\theta' = (\theta - A)$.

The fraction of first disturbances, F_j, that commence in the interval $(j-1)\Delta T$ to $j\Delta T$ after the laser triggers is given by

$$F_j = \int_{(j-1)\Delta T}^{j\Delta T} \phi(\theta) d\theta \tag{10}$$

where ΔT is any arbitrary time interval. If this value is chosen so that $\Delta T = A$, then

$$F_1 = \Delta T/(\tau + \Delta T)$$

$$F_j = \frac{1}{\tau + \Delta T} \exp(-2(j-2)\Delta T/\tau)[\tau + (j-2)\Delta T$$
$$-(\tau + (j-1)\Delta T) \exp(-2\Delta T/\tau)], \quad j = 2,3, \ldots . \tag{11}$$

Similarly, the fraction of subsequent disturbances, S_j, that commence in the interval $(j-1)\Delta T$ to $j\Delta T$ after the commencement of any previous disturbance is given by

$$S_j = \int_{(j-1)\Delta T}^{j\Delta T} f(t) dt \tag{12}$$

and thus

$$S_1 = 0$$

$$S_j = \exp(-2(j-2)\Delta T/\tau)[1 + 2(j-2)\Delta T/\tau$$
$$-(1 + 2(j-1)\Delta T/\tau) \exp(-2\Delta T/\tau)], \quad j = 2,3, \ldots . \tag{13}$$

The method of maximum likelihoods, described in a number of texts (e.g., Benjamin and Cornell, 1970), was used to obtain estimates of τ, $\hat{\tau}$, from Eqs. 8 and 9. This technique was chosen since it can easily be adapted to include censored data. The method is based on the result that the probability of an observation t_i from a population of frequency distribution $f(t,\tau)$ is $f(t_i,\tau)dt$. Thus the likelihood of a particular sequence of n observations, $L(t_1,t_2 \ldots . t_n:\tau)$, is given by

$$L(t_1,t_2 \ldots . t_n:\tau) = \prod_{i=1}^{n} f(t_i,\tau)dt. \tag{14}$$

The maximum likelihood estimate of τ is that value $\hat{\tau}$ that maximizes L. It is, however, usual to maximize the logarithm of L since the two maxima will occur for the same $\hat{\tau}$. Thus $\hat{\tau}$ is given by

$$\frac{d}{d\tau}\left[\sum_{i=1}^{n} \ln f(t_i,\tau)\right] = 0. \tag{15}$$

The probability of an event not occurring within the time interval 0 to T_i is given by

$$\int_{T_i}^{\infty} f(t,\tau)dt = 1 - F(T_i,\tau). \tag{16}$$

Thus the likelihood function in the case where some observations are censored takes the form

$$L(t_1,t_2 \ldots . t_n,T_1,T_2 \ldots . T_m:\tau)$$
$$= \prod_{i=1}^{n} f(t_i,\tau)dt. \prod_{i=1}^{m} [1 - F(T_i,\tau)]. \tag{17}$$

Hence, the problem reduces to finding $\hat{\tau}$ such that

$$\frac{d}{d\tau}\left[\sum_{i=1}^{n} \ln f(t_i,\tau) + \sum_{i=1}^{m} \ln(1 - F(T_i,\tau))\right] = 0. \tag{18}$$

The value of $\hat{\tau}$ is approximately normally distributed with a variance $v(\hat{\tau})$ given by

TABLE 2. RESULTS FOR AN AQUEOUS DROP GROWING IN TOLUENE CONTAINING 3 VOL % DIACETONE ALCOHOL

Position	Disturbance Type	A, ms	$\hat{\tau}$, ms	SD($\hat{\tau}$), ms
Near Apex	First	12	71.9	5.2
	Second	12	123	5.7
	Third	12	199	10
Near major diameter	First	28	136	6.4
	Second	28	212	7.7
	Third	28	207	9.6
Near nozzle	First	40	175	12
	Second	40	200	10
	Third	40	220	13

SD($\hat{\tau}$) = standard deviation of $\hat{\tau}$; D_N = 0.417 cm, v_N = 0.920 cm/s, Re_N = 42.

$$v(\hat{\tau}) = -1 \Bigg/ \frac{d^2 \ln L}{d\tau^2} \tag{19}$$

where the second derivative is evaluated at $\hat{\tau}$ (Benjamin and Cornell, 1970).

The curves corresponding to Eqs. 11 and 13 in Figures 4, 5, and 6 were based on $\hat{\tau}$ values found by solution of Eq. 18. The ordinates have been converted from fractional values by multiplying by the total number of observations, some of which occurred at longer time intervals than included in the figures.

DISCUSSIONS OF THE RENEWAL MEASUREMENTS

Equations 11 and 13 reproduce the general trends in the data shown in Figures 4, 5, and 6 and to this extent would appear to offer a useful starting point for representing the behavior of droplet surfaces. It must be remembered, however, that the measurements are specific to one particular system and that there is still a measure of uncertainty attached to the numerical values of both A and τ. Thus, for example, Figure 4 indicates that too many apparent first disturbances were recorded immediately after the laser triggered. The explanation probably lies in the tracer tests described earlier, which detected an occasional symmetrical expansion of the colored spot on a stationary droplet in the absence of mass transfer. If the same effect were present under conditions of mass transfer, there would be a consequent inflation in the number of first disturbances recorded near $j = 0$. Rather than attempt to distinguish the laser-induced disturbances from those due to mass transfer, the problem was compensated for by neglecting all first disturbances recorded at times less than the value of A determined from measurements of subsequent disturbances. Thus both the maximum likelihood estimate of τ and Eq. 11 in Figure 4 were based on an apparent number of observations equal to the number of observations at times greater than A multiplied by $(\hat{\tau} + A)/\hat{\tau}$. This factor arises from the result that

$$\int_A^\infty \phi(\theta) d\theta = \hat{\tau}/(\hat{\tau} + A), \tag{20}$$

where $\phi(\theta)$ is given by Eq. 9.

All values of A, the estimated minimum duration of a roll cell, were determined by visual observations of the cine recordings of second and subsequent disturbances. There is, therefore, a small but finite uncertainty in these values, inasmuch as from a statistical point of view the number of recorded observations was probably on the low side. Furthermore, it must be remembered that by their very nature, the observations can suffer from censoring since the droplet will always detach from the nozzle before the nth disturbance can become manifest; in this connection, the value of n will be determined by the properties of the system and the rate of droplet formation.

Notwithstanding these limitations, the maximum likelihood estimates of τ for all three regions of the droplet surface are summarized in Table 2, where a number of trends are apparent. Thus both the duration of a disturbance and the time interval between successive disturbances increase with distance from the droplet apex. Furthermore, for a fixed initial position of the tracer spot, the time constant $\hat{\tau}$ tends to increase for subsequent instabilities.

The physical picture that has emerged to date is one of irregular exchange of the fluid in an otherwise laminar interface with that at the base of the roll cells. Furthermore, since the measurements recorded in Table 2 were all determined at $Re_N > 35$, the droplets would be expected to be circulating so that a slow convective pattern from the droplet apex to the nozzle would be superimposed upon the roll cell phenomenon. The net effect is likely to result in an increasing solute concentration at the base of the roll cells and flatter concentration profiles normal to the interface as one approaches the vicinity of the nozzle.

The model of Sternling and Scriven (1959) implies that the growth constant of a Marangoni instability is not only a function of the physical properties of the system and the disturbance scale but also decreases for lower values of the initial undisturbed concentration gradient. The present implication (Table 2) that roll cells have a longer duration near the nozzle is therefore not unexpected. Furthermore, these authors also concluded that high concentration gradients promoted interfacial instability, and thus the trend in $\hat{\tau}$ values with position is also expected.

Implicit in these explanations is the assumption that solute levels at the base of the roll cells are influenced primarily by exchange with the surface layers. Thus a restriction is placed on the rate of transport into the drop interior. The explanation also highlights a limitation in the present data since it emphasizes that the stability of a surface element depends partly on the concentration at its base. Furthermore, this concentration is influenced by the number of previous disturbances in the relevant region of the droplet surface during the interval since its creation near the apex. Thus the present procedure of labeling surface elements at a constant position and stage of drop growth does not necessarily insure that all these elements have similar concentration gradients, since the number of previous disturbances is stochastic. It therefore follows that surface elements selected on the present basis need not all belong to the same population, and it is for this reason that more elaborate expressions for two frequency functions, described by Eqs. 5 and 6, f_d and f_i, have not been attempted. Thus, while the present model does not claim to be an accurate mechanistic description of solute-induced disturbances, it does on the other hand indicate the probable factors upon which surface renewal rates depend.

A consequence of the positional dependence of both A and $\hat{\tau}$ is the need to integrate point values of the mass transfer flux over the droplet profile in order to reflect the true transfer rate over the droplet as a whole. The applications of these findings to simultaneous measurements of mass transfer and surface renewal rates are reported in Part II of this paper.

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Notation

A = estimated minimum duration of a roll cell, s
D = diameter, m

$F(t)$ = cumulative residence time distribution, equal to the fraction of the surface that suffers a disturbance within a time t

$F(t,\tau)$ = population cumulative frequency distribution

F_j = fraction of first disturbances that commence in the interval $(j-1)\Delta T$ to $j\Delta T$ after the laser triggers

$f(t)$ = residence frequency density function, s^{-1}

$f_d(t)$ = residence frequency density function of elements within a disturbance, s^{-1}

$f_i(t)$ = residence frequency density function of elements in the interval between the end of one disturbance and the commencement of the next, s^{-1}

$f(t,\tau)$ = population frequency density function, s^{-1}

j = integer 2,3 . . .

Re_N = nozzle Reynolds number defined as $D_N v_N \rho_d/\mu_d$

S_j = fraction of subsequent disturbances that commence in the interval $(j-1)\Delta T$ to $j\Delta T$ after the commencement of any previous disturbance

s = fractional rate of surface renewal, s^{-1}

T^* = mean residence time, s

T_i = sample value from a population with cumulative frequency function $F(T,\tau)$, s

ΔT = arbitrary time interval, s

t = time measured from the moment of creation of a surface element, s

t' = defined as $t - A$, s

t_i = sample value from a population with frequency density function $f(t,\tau)$

v = average fluid velocity, m/s

Greek Letters

θ = age, s

θ' = defined as $\theta - A$, s

μ = fluid viscosity, kg/ms

ρ = fluid density, kg/m^3

τ = reciprocal fractional rate of surface renewal, s

$\hat{\tau}$ = maximum likelihood estimate of τ, s

τ_d = reciprocal fractional rate at which disturbed elements pass from a disturbance, s

τ_i = reciprocal fractional rate at which undisturbed elements become disturbed, s

$\phi(\theta)$ = age frequency density function

Subscripts

d = dispersed phase

N = nozzle

LITERATURE CITED

Benjamin, J. R., and C. A. Cornell, *Probability, Statistics and Decisions for Civil Engineers*, McGraw-Hill, New York (1970).

Burkhart, L., P. W. Weathers, and P. C. Sharer, "Mass Transfer and Internal Circulation in Forming Drops," *AIChE J.*, **22**, 1,090 (1976).

Calvert, J. G., and J. N. Pitts, *Photochemistry*, Wiley, New York, 783 (1964).

Danckwerts, P. V., "Significance of Liquid-Film Coefficients in Gas Absorbtion," *Ind. Eng. Chem. Eng. Proc. Dev.*, **43**, 1,460 (1951).

———, "Gas Absorbtion Accompanied by Chemical Reaction," *AIChE J.*, **1**, 456 (1955).

Davies, J. T., and W. Khan, "Surface Clearing by Eddies," *Chem. Eng. Sci.*, **20**, 713 (1965).

Goldish, L. H., J. A. Koutsky, and R. J. Adler, "Tracer Introduction by Flash Photolysis," *Chem. Eng. Sci.*, **20**, 1,011 (1965).

Highbie, R., "The Rate of Absorbtion of a Pure Gas into a Still Liquid During Short Periods of Exposure," *Trans. AIChE*, **31**, 365 (1935).

Humphrey, J. A. C., R. L. Hummel, and J. W. Smith, "Experimental Study of the Internal Fluid Dynamics of Forming Drops," *Can. J. Chem. Eng.*, **52**, 449 (1974a).

Humphrey, J. A. C., et al., "Light-Induced Disturbances in Photochromic Flow Visualization," *Chem. Eng. Sci.*, **29**, 308 (1974b).

Kanner, B., and J. E. Glass, "Surface Viscosity and Elasticity," *Ind. Eng. Chem.*, **61**, 31 (1969).

Kishinevski, M. Kh., and A. V. Pamfilov, "The Kinetics of Absorbtion," *J. App. Chem. USSR*, **22**, 1,173 (1949).

Koppel, L. B., R. D. Patel, and J. T. Holmes, "Statistical Models for Surface Renewal in Heat and Mass Transfer. I: Dependence of Average Transport Coefficients on Age Distribution," *AIChE J.*, **12**, 941 (1966).

Lewis, W. K., "The Principles of Countercurrent Extraction," *Ind. Eng. Chem.*, **8**, 825 (1916).

Lewis, W. K., and W. G. Whitman, "Principles of Gas Absorbtion," *Ind. Eng. Chem.*, **16**, 1,215 (1924).

Perlmutter, D. D., "Surface Renewal Models in Mass Transfer," *Chem. Eng. Sci.*, **16**, 287 (1961).

Popovich, A. T. and R. L. Hummel, "A New Method for Nondisturbing Turbulent Flow Measurements Very Close to a Wall," *Chem. Eng. Sci.*, **22**, 21 (1967).

Sawistowski, H., "Recent Advances in Liquid-Liquid Extraction," *Interfacial Phenomena*, C. Hanson, Ed., Pergamon Press, Ch. 9 (1971).

Sawistowski, H., and G. E. Goltz, "The Effect of Interface Phenomena on Mass Transfer Rates in Liquid-Liquid Extraction," *Trans. Inst. Chem. Engrs.*, **41**, 174 (1963).

Sternling, C. V., and L. E. Scriven, "Interfacial Turbulence: Hydrodynamic Instability and the Marangoni Effect," *AIChE J.*, **5**, 514 (1959).

Thornton, J. D., and T. J. Anderson, "Surface Renewal Phenomena in Liquid-Liquid Droplet Systems with and without Mass Transfer," *Int. J. Heat Mass Transfer*, **24**, 1847 (1981).

Van Voorhis, J. J., J. V. Cartmell, and P. Y. Hsieh, "Surface Activity of Some Merocyanines and Spiropyrans at Liquid-Liquid Interaces," *J. Coll. Sci.*, **20**, 8 (1970).

Zwietering, Th. N., "The Degree of Mixing in Continuous Flow Systems," *Chem. Eng. Sci.*, **11**, 1 (1959).

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