Surface Phenomena and Mass Transfer Rates in Liquid-Liquid Systems: Part 2

Simultaneous measurements of mass transfer rates to quasisteady-state pendant aqueous droplets and rates of surface renewal due to Marangoni effects have been carried out using the water/toluene system with acetone as solute. The surface renewal measurements were made with the photochromic dye tracer technique reported earlier (Thornton and Anderson, 1981; Thornton et al., 1985).

Both the mass transfer coefficients and the rates of surface renewal have been shown to be dependent upon the age of the droplet interface and the solute concentration in the continuous phase. Thus, coefficients of a young droplet are high initially, but decrease with time and approach a constant value, dependent upon solute concentration, as the interface ages.

This parallel decrease in both interfacial (Marangoni) activity and transfer rates with time has also been observed (Rogers et al., 1987) with inorganic solutes such as uranyl nitrate and has implications for contactor design.

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Introduction

The transfer of an undistributed solute across a liquid-liquid interface frequently gives rise to spontaneous perturbations at the phase boundary. These so-called Marangoni effects have been attributed (Sternling and Scriven, 1959) to interfacial tension gradients produced by local variations in solute concentration along the interface.

The mass transfer rates accompanying such phenomena are higher than would be expected solely on the basis of molecular diffusion, and Sawistowski and Goltz (1963) demonstrated that the coefficients increased rapidly when the solute driving force exceeded a critical value. This was attributed to the onset of interfacial turbulence at the critical driving force and was supported qualitatively by Schlieren photography.

Bakker et al. (1966) reported a study of the convection cells formed at the interface during the extraction of acetic acid from ethylene glycol and from isobutyl alcohol, and concluded that the linear size and penetration depth were of the same order of magnitude and estimated that the mass transfer rates were increased due to the convection cells by a factor of three or more. In a subsequent study (Bakker et al., 1967), it was shown that the ratio of measured mass transfer rates to those predicted by the penetration theory was a function of driving force. Furthermore, the ratio was reported to increase from unity to a value of between two and three, as the driving force was increased. Abnormally high transfer rates accompanying interfacial activity have also been reported by Lewis (1954), Sherwood and Wei (1957), Olander and Reddy (1964), Berg and Haselberger (1970), Lode and Heideger (1970), and Takenchi and Numta (1977).

The time-dependent nature of these interfacial effects has been reported by Maradous and Sawistowski (1964), and Orell and Westwater (1961, 1962), who noted the change in pattern with time ranging from polygonal cells to ripples before disappearing as equilibrium was reached. Schlieren studies of interfacial turbulence in drops suspended from a nozzle also showed that turbulence produced during solute transfer decayed rapidly with time (Naikaike and Takaki, 1979). Perturbations of this kind have been shown to increase in both frequency and duration with solute concentration (Naikaike et al., 1971).

The time-dependent nature of interfacial effects has also been observed in quasisteady-state droplet systems undergoing mass transfer using both organic (Javed and Thornton, 1984) and inorganic solutes (Rogers et al., 1987). In these cases, equilib-

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rium was never reached and the progressive decrease in interfacial activity was related in an unknown way to the "age" of the droplet interface.

Although interfacial effects accompanying solute transfer have been the subject of several analyses (Sternling and Scriven, 1959; Ruckenstein, 1968; Gross and Hixson, 1969a,b; Naikaike et al., 1971; Imaishi and Fujinawa, 1974), no generalized model has yet evolved which would enable the effects of interfacial activity upon transfer rates to be predicted quantitatively. Such analyses are complicated by superimposed effects such as convective flow induced by density gradients. Berg and Morig (1969) demonstrated that such gradients might themselves produce convective flows or they might retard or enhance the convection generated by the Marangoni effect. A further complication may arise from the heat of solution accompanying the transfer of solute across an interface, since this can influence both the interfacial tension and any density gradients (Heines and Westwater, 1972; Ortiz and Sawistowski, 1973, 1975; Davies and Thornton, 1977).

The direct observation and quantitative measurement of surface renewal have not been possible in the past due to lack of an experimental technique which would enable the eddy life time distribution during the renewal process to be evaluated. Very recently, a photochromic dye tracer technique has been shown to be suitable for this purpose (Thornton and Anderson, 1981; Thornton et al., 1985) and has been employed to study the surface renewal characteristics of growing, pendant droplets. Briefly, the procedure makes use of a finely focussed ultraviolet laser pulse to induce a local color change in a chemical tracer dissolved in the aqueous droplet, thereby labeling a very small element of the droplet surface. The subsequent history of the spot is then recorded photographically on high-speed cine film and the time intervals between successive disturbances experienced by the spot determined from a frame-by-frame analysis of the film. The data so obtained may then be interpreted in terms of the age or residence time distribution functions of the liquid surface elements.

The same technique has been used in the present paper to study the surface behavior of a hemispherical quasisteady-state aqueous droplet immersed in toluene with different concentrations of acetone transferring from the toluene to the droplet. The droplet was formed at the tip of a glass nozzle by a continuous feed of aqueous phase containing the tracer, and a constant volume was maintained by withdrawing the aqueous liquor from the droplet via an outer concentric nozzle.

Simultaneous mass transfer and surface renewal rates have been measured by this means in order to show up interactions between the two phenomena. Similar experimental arrangements were used by Constant and Calvert (1963), and Panno and Calvert (1965) to study the effect of forced circulation on mass transfer in a gas-liquid system and later by Burkhart et al. (1976) in a liquid-liquid system. The present procedure, however, had the advantage that it allowed the determination of solute concentration in the outgoing dispersed phase as a function of time, whereas the previous work only allowed time-averaged mass transfer rates to be measured.

Experimental Work

Extraction system

Laboratory distilled water containing the dissolved photochemical tracer was used as the dispersed phase and "Analar" grades of toluene and acetone were employed as the continuous phase and solute, respectively. The constituents of the tracer and the method of preparation have been described previously (Thornton et al., 1985). As a precaution, the concentration of tracer was reduced by 50% in order to avoid the likelihood of agglomeration of the color complex formed on irradiation although this had not been observed in the past.

Apparatus

A schematic diagram of the flow system is shown in Figure 1. All the essential apparatus was constructed of glass. The concentric nozzle (I) used to form the constant volume droplet was constructed from two glass tubes; the inner tube measured 1.5 mm ID and 7.0 mm OD while the corresponding measurements of the outer tube were 10.0 mm ID and 11 mm OD.

The continuous phase was contained in a cylindrical glass cell

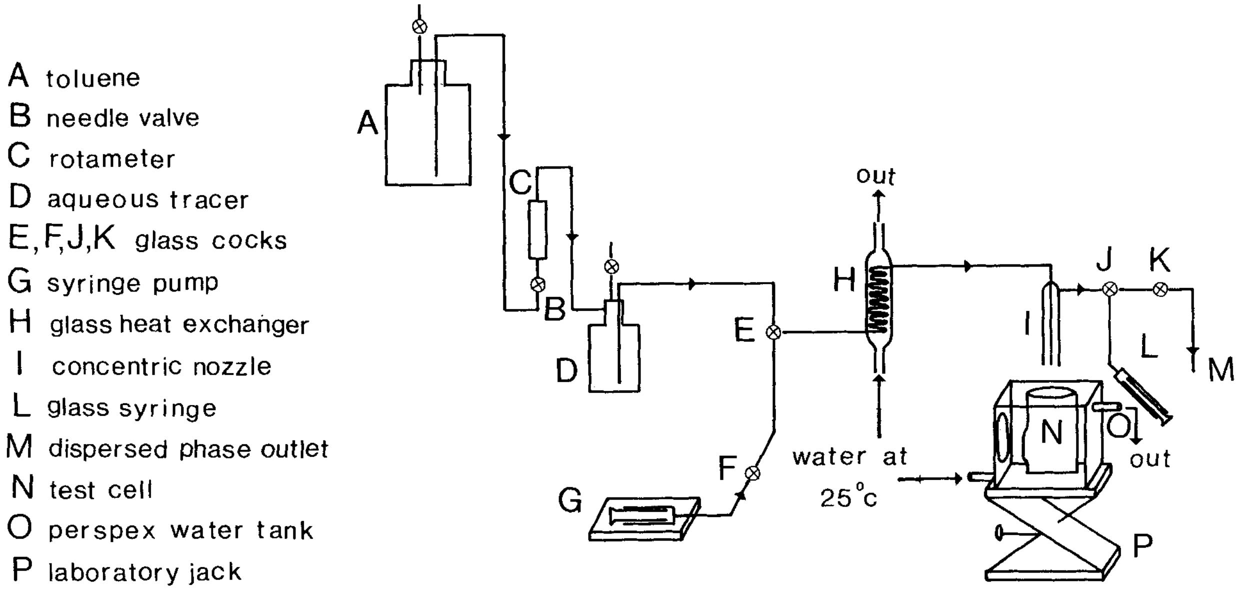

Figure 1. Experimental arrangement.

(N), 10 cm high and 8 cm diameter, and was equipped with an optically flat window which transmitted the UV laser pulse and allowed an undistorted view of the droplet at the tip of the nozzle. The cell was placed in a constant temperature bath (O) which itself was supported by a laboratory jack so that the nozzle (primed with aqueous phase) could be immersed in the continuous phase just prior to a run.

The aqueous phase was fed to the nozzle from a glass container (D) by displacement with toluene from an overhead aspirator (A). The toluene flow rate was controlled by a needle valve (B) and a flowmeter assembly (C). Prior to entering the nozzle, the aqueous phase passed through a glass heat exchanger (H) in order to bring it to the same temperature (25°C) as the continuous phase. Aqueous liquor from the droplet was withdrawn via a capillary line by siphoning, the flow rate being controlled by adjusting the level of the outlet leg (M) with a micrometer screw. The droplet was viewed continuously with a video camera and the magnified image monitored against a graticule screen so that any changes in the droplet profile (and hence volume) could be compensated immediately by appropriate adjustments of the flow rates. An auxiliary syringe (L) enabled the nozzle annulus and the outlet line to be filled with continuous phase before each run.

Provision was also made for the injection of aqueous phase at a low and controlled rate directly into the feed line so that a fresh droplet could be formed at the nozzle without disturbing the inlet and outlet flows which had already been adjusted to constant droplet volume conditions. This additional temporary input was provided from a 50 mL glass syringe driven electrically by a microsyringe pump (G). This was isolated immediately the droplet had attained a hemispherical shape.

Laser and photographic arrangements

A small area of droplet surface was irradiated by an ultraviolet pulse from a ruby laser which was fitted with a frequency doubler in order to provide a light pulse in the UV wavelength. The laser beam was finely focused on the desired point on the droplet surface by a quartz lens of focal length 30 cm.

The illumination for photographing the colored spot on the droplet surface was provided by two 500-W photoflood lights. The light passed through a red diffusing filter which filtered out the UV wavelengths so that the photochromic tracer was not activated by this source of illumination.

The droplet and the tracer spot were viewed by a video camera through a mirror mounted at 45° to the laser beam. Through a second mirror mounted similarly, the behavior of the spot was filmed at a camera speed of 250 frames per second.

Sampling and analysis

Mass transfer measurements were based on the concentration of acetone in the aqueous phase flowing continuously out of the droplet. Since the sampling point was located some way downstream, the liquid leaving the droplet took finite time to reach the sample point. This delay was measured using a stimulus-response technique, and the mean residence time was found to be exactly 60 seconds; this correction was then applied to all the sample times. Each sample was approximately 0.3 mL and was collected over a period of 3 seconds.

Acetone analyses in the aqueous liquor were made by gas chromatography using a glass column packed with 15% carbowax 20M with a chromosorb W 80–100 mesh support.

Procedure

Mass transfer measurements were carried out using three different concentrations of acetone in toluene, *viz.*, 0.5%, 1% and 5% by volume. The concentration of acetone in the aqueous feed to the droplet was always zero.

Simultaneous mass transfer and surface renewal measurements were made using 5% acetone; the remaining solute concentrations were employed to investigate surface renewal only and to differentiate the droplet surface behavior from that for the 5% concentration.

In each case, the droplet surface was labeled in the middle region and at exactly the same age of the interface except in one run at 5% concentration, when the spot was created after 10

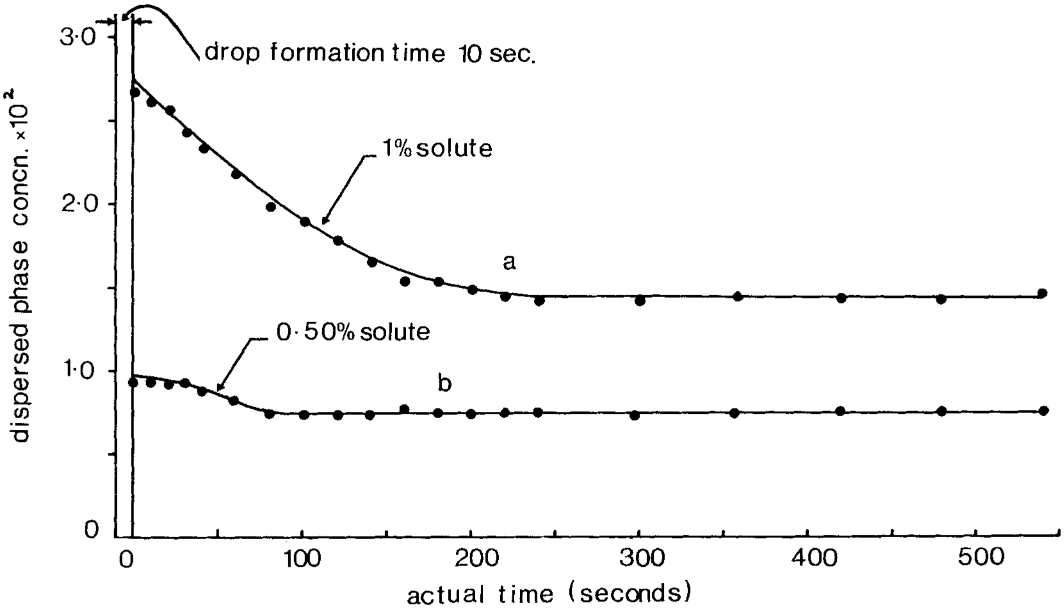

Figure 2. Dispersed-phase concentration vs. time for 0.50% and 1.0% solute concentrations (expressed as vol. %).

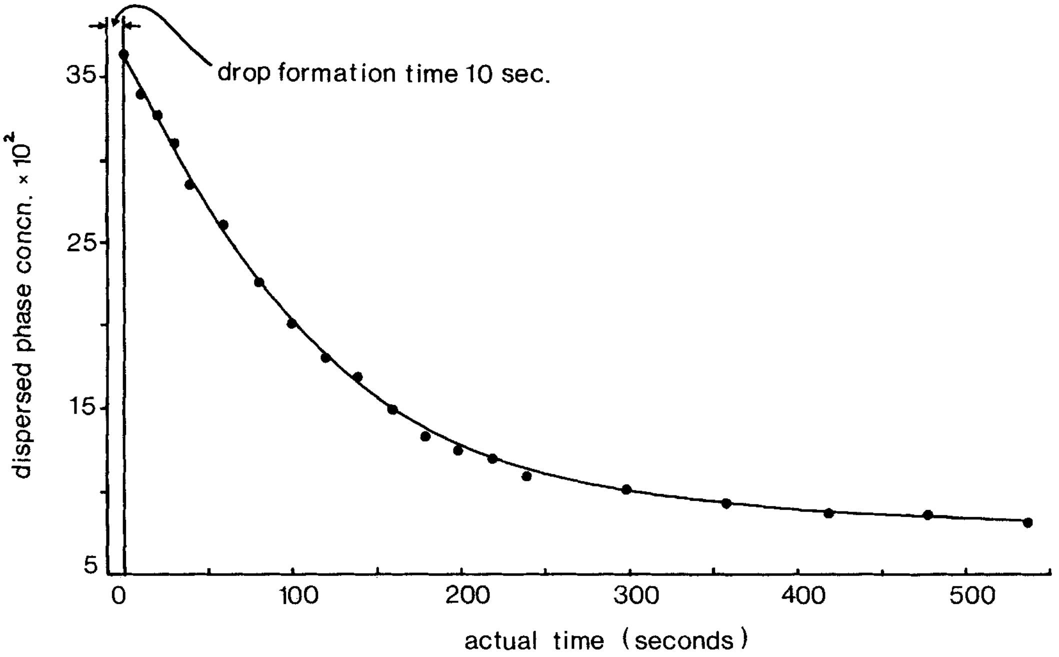

Figure 3. Dispersed-phase concentration vs. time for 5.0% solute concentration (expressed as vol. %).

minutes in order to observe the effect of age of the interface on surface mixing phenomena.

Before commencing each run, all the glass apparatus was cleaned by soaking for several hours in chromic acid; it was then thoroughly washed in distilled water and dried. The aqueous tracer solution was prepared shortly before each run and the aqueous and solvent phases were mutually saturated before use.

Each run was commenced by carefully filling the inlet and outlet lines with the aqueous solution of tracer so that all air bubbles were excluded. The nozzle was then immersed in the continuous toluene phase by raising the jack. The droplet was formed by allowing the aqueous liquor to flow through the main inlet feed line, while simultaneously initiating the flow out of the droplet by opening the outlet line and adjusting the flow rate so as to obtain a hemispherical droplet of constant size. A feed flow rate of 385 mL/h was used throughout. Having established constant flow conditions, the actual run was started by forming a new droplet at the nozzle by supplying an additional flow of 100 mL/h to the feed line by means of the syringe pump. The additional flow was stopped as soon as the droplet attained the predetermined hemispherical size and, at that instant, the time was taken as zero. Exactly ten seconds later, a laser pulse was triggered to label an element of the droplet surface and the cine recording was started to record the history of the spot. Sampling of the outlet aqueous phase commenced 60 seconds later in order to allow for the holdup in the sample line.

Between 20 and 25 samples were taken over a ten-minute period during each mass transfer run and each run was repeated at least three times. The samples were then analyzed for acetone as described earlier.

Results

Mass transfer

The concentration of acetone in the droplet is plotted as a function of time in Figure 2 for initial concentrations of 0.5% and 1.0% in the toluene phase; the corresponding curve for 5% concentration is shown in Figure 3.

The values of the corresponding instantaneous overall mass transfer coefficients based on the dispersed phase were calculated from material balance considerations and the resulting K_{od} vs. time curves are shown in Figure 4.

When mass transfer is not accompanied by any interfacial effects, the theoretical relationship between concentration and time can be derived from an unsteady-state material balance to give:

$$c = [K_{od} \cdot A_d \cdot c^* / (K_{od} \cdot A_d + F)] \cdot \{1 - \exp[-(K_{od} \cdot A_d + F)t/V_d]\} \quad (1)$$

This expression describes transfer into the droplet with forced circulation which is dependent on the flow rate F. It may be noted that, when $F = 0$, the equation reduces to the usual expression for a freely moving droplet

$$c = c^* \{1 - \exp[-K_{od} \cdot A_d \cdot t/V_d]\} \quad (2)$$

Both of these expressions are based on the fundamental assumptions that the mass transfer coefficient is a sole function of the hydrodynamic conditions of the droplet and that, for any given set of conditions, the coefficient is constant and independent of time. Thus, in the absence of any flow inside the droplet, the mass transfer coefficient in both cases would assume the limiting value corresponding to a stagnant droplet. This condition is represented by the horizontal line AA′ in a diagram such as that shown in Figure 5. In the case of forced circulation, as in the present instance, the line AA′ would be displaced vertically to take into account the higher coefficient arising from hydrodynamic flow within the droplet. This situation is represented by the line BB′.

In the presence of interfacial turbulence, the present work has shown that the coefficient is initially enhanced considerably but

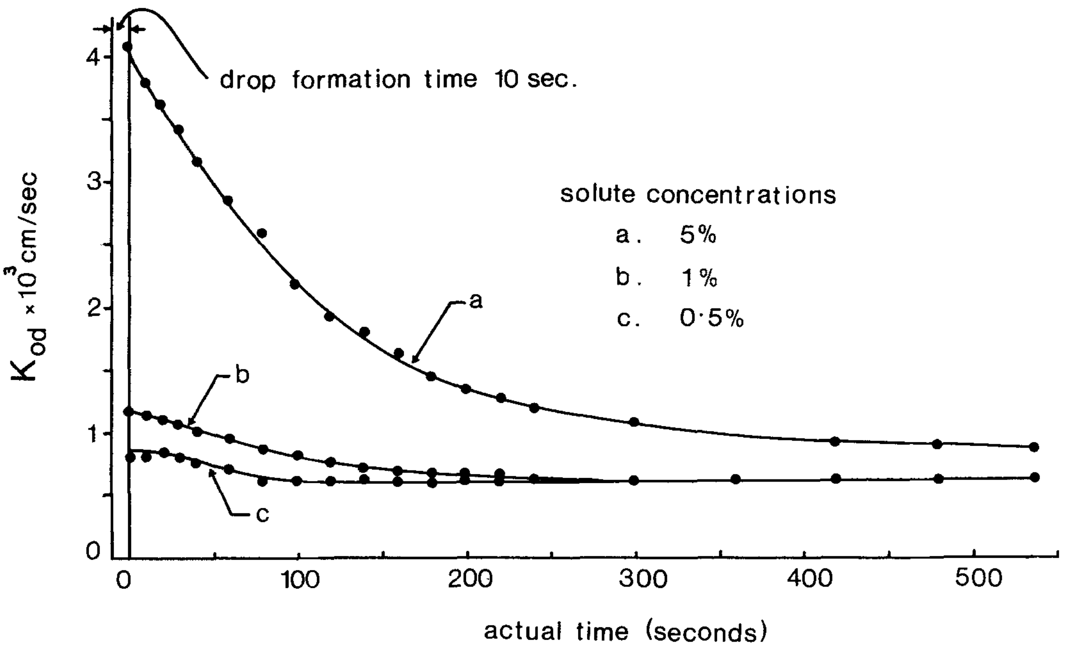

Figure 4. Overall dispersed-phase mass transfer coefficients vs. time for 0.50, 1.0 and 5.0% solute concentrations.

that the degree of enhancement decreases with time as the time interval between successive disturbances increases. Thus, in practice, the coefficient time dependence takes the form of curve CC′ shown in Figure 5. In this diagram, it is assumed that interfacial activity decays to a low but constant level after a sufficiently long period of time. Furthermore, since it is not unreasonable to suppose that the frequency and intensity of the interfacial disturbances would be dependent upon the mass flux, a family of curves might be anticipated which are dependent upon the initial solute concentration as shown in the diagram.

In each of the three initial solute concentrations studied, it was found that the enhancement in the mass transfer coefficient over its steady-state value decayed exponentially with time so that:

$$K_{od} = K_{ods} + (K_{od\max} - K_{ods}) \cdot e^{-mt} \tag{3}$$

where

K_{od} = observed overall dispersed phase mass transfer coefficient at any time t

K_{ods} = overall dispersed phase coefficient at steady state

$(K_{od\max} - K_{ods})$ = initial enhancement over the steady-state coefficient due to interfacial effects

m = decay constant

Equation 3 thus accounts for the effect of the interfacial disturbances over and above that due to the flow conditions within the droplet. Equation 3 has been fitted to each of the three sets of K_{od} vs. time curves shown in Figure 4 by the method of least squares and Figure 6 compares the experimental and best fit values of the coefficients. The constants in Eq. 3 are tabulated in Table 1.

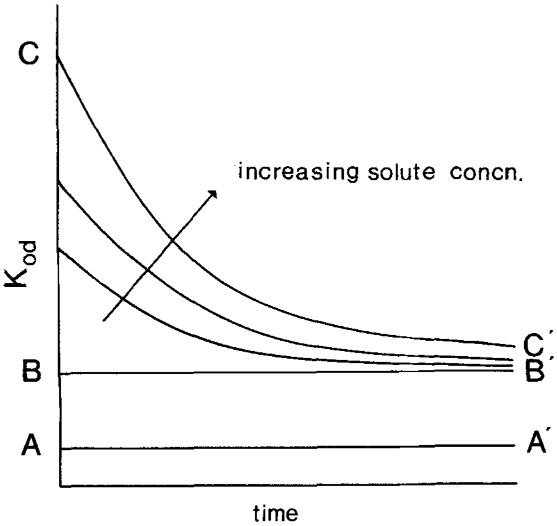

Figure 5. Model curves for K_{od} vs. time.

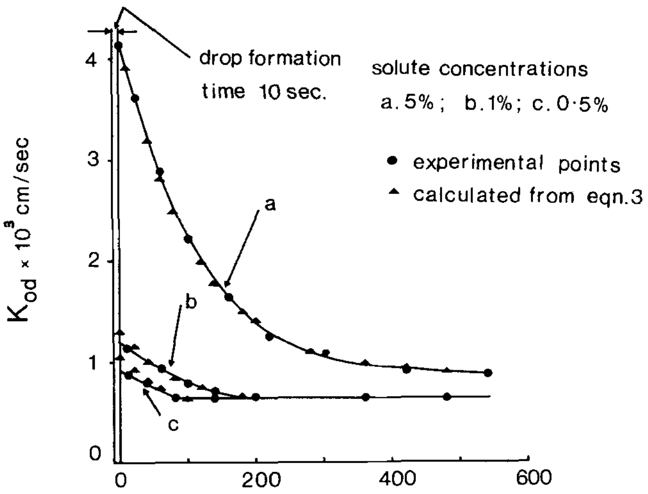

Figure 6. Experimental and fitted curves for K_{od} vs. time.

Table 1. Constants in Eq. 3

Solute Conc.	$(K_{od\,max}-K_{ods})$	m	Corr. Coeff.
0.5%	4.39×10^{-4}	0.0229	0.95
1.0%	6.91×10^{-4}	0.0141	0.98
5.0%	3.35×10^{-3}	0.0090	0.99

Surface renewal

The high-speed cine films obtained in the presence of mass transfer showed that the tracer spot experienced a sequence of violent disturbances which led to the disintegration of the spot. This behavior was found to be dependent upon the acetone concentration in the toluene phase and, for a given concentration, also on the age of the droplet interface. As the solute concentration was increased, the intensity of the disturbances increased considerably resulting in rapid dispersion of the spot. On the other hand, the intensity of the disturbances decreased rapidly as the interface aged, indicating the decay of interfacial turbulence with time.

In contrast to these observations, there was no indication of any disturbance to the tracer spot in the absence of mass transfer, even over an extended period of time. The behavior of the tracer spot under the different conditions studied is shown in Figures 7 to 11 which depict photographic sequences taken from typical runs.

Two sets of measurements were obtained from the cine record for the 5% acetone concentration, *viz.*, the time interval between the instant the spot was created, and the onset of the first dis-

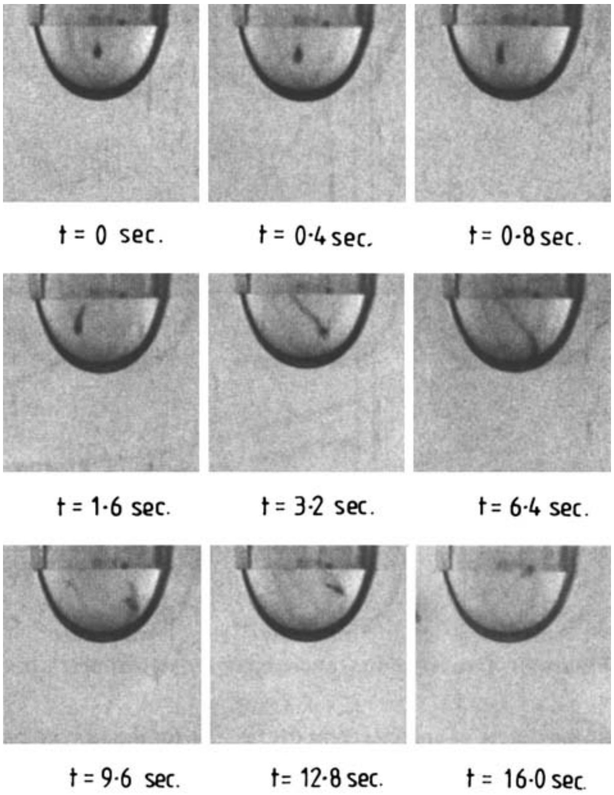
t = 0 sec. t = 0·4 sec. t = 0·8 sec.
t = 1·6 sec. t = 3·2 sec. t = 6·4 sec.
t = 9·6 sec. t = 12·8 sec. t = 16·0 sec.

Figure 7. Quasisteady-state drop of aqueous dye in toluene over a period of time in the absence of mass transfer.

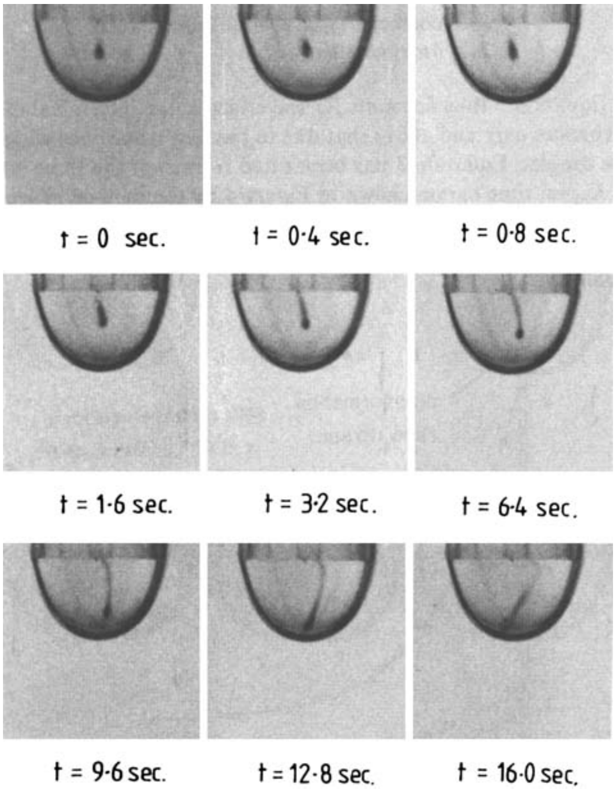
t = 0 sec. t = 0·4 sec. t = 0·8 sec.
t = 1·6 sec. t = 3·2 sec. t = 6·4 sec.
t = 9·6 sec. t = 12·8 sec. t = 16·0 sec.

Figure 8. Quasisteady-state aqueous drop containing 0.50% acetone over a period of time.

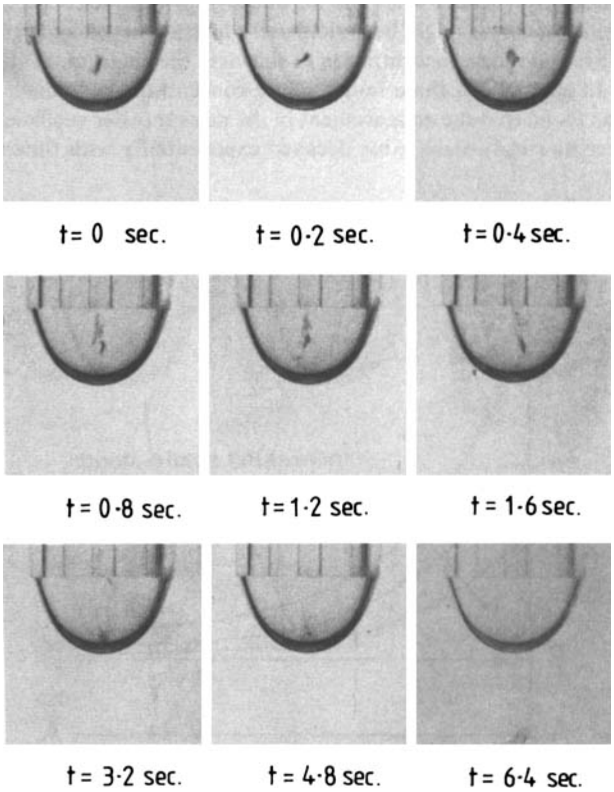
t = 0 sec. t = 0·2 sec. t = 0·4 sec.
t = 0·8 sec. t = 1·2 sec. t = 1·6 sec.
t = 3·2 sec. t = 4·8 sec. t = 6·4 sec.

Figure 9. Quasisteady-state aqueous drop containing 1.0% acetone over a period of time.

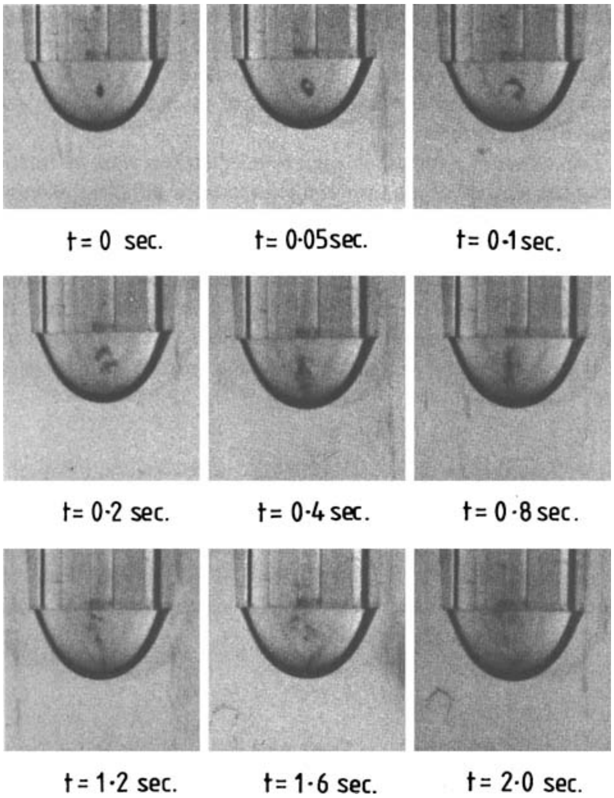

Figure 10. **Quasisteady-state aqueous drop containing 5.0% acetone over a period of time.**

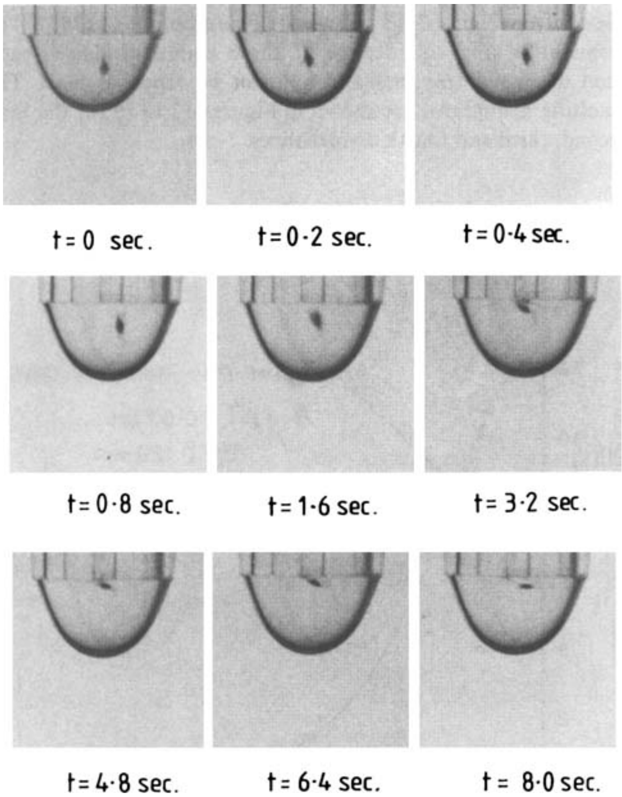

Figure 11. **Quasisteady-state aqueous drop containing 5.0% acetone but labelled 10 minutes after formation.**

turbance as well as the time intervals between subsequent disturbances. These measurements were used to evaluate the age distributions of the fluid eddies using the theoretical surface renewal model developed in Part 1 (Thornton et al., 1985). In Part 1, it was pointed out that interfacial disturbances were largely due to the formation of roll cells so that the duration of a disturbance might thus be equated to the lifetime of the associated roll cell. In the model, roll cells were assumed to have a minimum duration A before they terminated with a probability independent of time and determined only by the time constant of a first-order process. The time interval between consecutive disturbances (or equivalently between roll cells) was assumed to be represented by a second first-order process in series. On this basis, the theoretical equation for the surface age distribution function, $\phi(\theta)$, takes the form:

$$\phi(\theta) = \begin{bmatrix} \dfrac{1}{\tau + A} & 0 \leqslant \theta \leqslant A \\ \dfrac{1}{\tau + A}(1 + 2\theta'/\tau)\exp - (2\theta'/\tau) & 0 < \theta' < \infty \end{bmatrix} \tag{4}$$

where $\theta' = \theta - A$, and A is the estimated minimum duration of a roll cell.

Equation 4 may be used to estimate the values of the mass transfer coefficients for different surface age distributions of the droplet. Thus, the rate of solute transfer into the total surface, $\overline{N}$, is given by:

$$\overline{N} = \int_0^\infty N\phi(\theta) \cdot d\theta \tag{5}$$

where N is the instantaneous flux. In the present circumstances, there are two contributions to this expression:

1)Transfer during the minimum life of a roll cell

$$= \int_0^A N\phi(\theta) \cdot d\theta$$

2) Transfer in the interval between roll cells

$$= \int_A^\infty N\phi(\theta) \cdot d\theta$$

The second quantity is easily evaluated, since the surface is quiescent and transfer must proceed by molecular diffusion. Extraction during a disturbance, however, is complicated by the movement of fluid so that the situation may not correspond to diffusion into infinite media, particularly since the presence of a roll cell implies convection normal to the interface. This flow will tend to increase the transfer rate so that any model based on diffusion alone can be expected to provide an underestimate of the true rate.

Thus, a first low estimate of the mass transfer coefficient can be obtained by assuming molecular diffusion into an infinite, planar medium in the absence of an interfacial resistance so that N is given by:

$$N = (c^* - c_o)(\mathcal{D}/\pi\theta)^{0.5} \tag{6}$$

where c^* is the interfacial solute concentration. If it is further assumed that the surface absorbs solute during a disturbance as if it were stationary (this is equivalent to approximating the duration of a roll cell to an instantaneous instability followed by a delay during which the surface is quiescent), then:

$$\int_0^A N\phi(\theta)d\theta = 2(c^* - c_o)(\mathcal{D}A/\pi)^{0.5}/(\tau + A) \qquad (7)$$

and

$$\int_A^\infty N\phi(\theta)d\theta = \{(c^* - c_o)(\mathcal{D}/\pi)^{0.5}/(\tau + A)\}\{A^{0.5} + (\pi\tau/2)^{0.5} \cdot [1 - \mathrm{erf}(2A/\tau)^{0.5}](3/2 - 2A/\tau) \cdot \exp(2A/\tau)\} \qquad (8)$$

where $\phi(\theta)$ is given by Eq. 4 and the film mass transfer coefficient is defined by

$$\bar{N} = k(c^* - c_o) \qquad (9)$$

Combining Eqs. 5, 7, 8 and 9 gives the result:

$$k = (\mathcal{D}/\pi)^{0.5}[1/(\tau + A)]\{3A^{0.5} + (\pi\tau/2)^{0.5}[1 - \mathrm{erf}(2A/\tau)^{0.5}] \cdot (3/2 - 2A/\tau) \cdot \exp(2A/\tau)\} \qquad (10)$$

Clearly, there are two film coefficients to be considered and $\mathcal{D}$ is the solute diffusivity in the relevant phase. The overall coefficient is then computed in the usual manner.

An alternative estimate of k can be derived by assuming fresh surface at the end of a disturbance. The contribution to solute transfer in the interval $0 \leq \theta \leq A$ remains unaltered while N for $\theta > A$ is given by:

$$N = (c^* - c_o)[\mathcal{D}/\pi(\theta - A)]^{0.5} \qquad (11)$$

since the surface has only been exposed to solute for a period $(\theta - A)$. Thus

$$\int_A^\infty N\phi(\theta)d\theta = 3(c^* - c_o)(\mathcal{D}\tau/2)^{0.5}/2(\tau + A) \qquad (12)$$

and

$$k = (\mathcal{D})^{0.5}[1/(\tau + A)][2(A/\pi)^{0.5} + 3(\tau/2)^{0.5}/2] \qquad (13)$$

Either Eq. 10 or 13 may be employed to estimate the film coefficients for each phase provided that the values of τ as well as those of A are known. The direct experimental measurement of A is not available and must be assumed for any given set of observations. The value of τ, on the other hand, can be estimated from the measured distributions of time intervals between successive disturbances.

Table 2. Estimated Coefficients

A	$K_{od} \times 10^3$, cm/s Eq. 10	Eq. 13	Eq. 14
0.000	4.37	4.31	4.59
0.004	4.34	4.90	4.57
0.008	4.33	5.08	4.55
0.012	4.32	5.22	4.53
0.016	4.31	5.33	4.52
0.020	4.31	5.41	4.51
0.024	4.31	5.47	4.50
0.028	4.31	5.54	4.49
0.032	4.30	5.59	4.47
0.036	4.30	5.63	4.46
0.040	4.30	5.66	4.45

The values of τ for use in the above equations were estimated using the method of maximum likelihoods for different assumed values of A in the range 0 to 0.4 seconds for each of the disturbances. In most instances, the tracer spot underwent up to four disturbances before it was completely dispersed. For each disturbance and for a given value of A in the specified range, the film coefficients were calculated from Eqs. 10 and 13. In addition, the coefficients were also calculated using Higbie's equation.

$$k = 2(\mathcal{D}/\pi\theta)^{0.5} \qquad (14)$$

but replacing the time of contact between the two phases, θ, by the total residence time $(\tau + A)$. Diffusivities were estimated by the method of Wilke and Chang (1955). In each case, the overall dispersed-phase mass transfer coefficients were calculated from the usual expression:

$$K_{od} = (k_c k_d)/(k_c + H \cdot k_d) \qquad (15)$$

and were averaged over the respective disturbances in each case. The comparison between the estimated and the experimental coefficients is shown in Table 2. The figures in Table 2 compare with experimental values of K_{od} ranging from 3.73×10^{-3} to 4.09×10^{-3}. The likelihood estimates of τ were also used to compute the frequency histograms for first and subsequent disturbances from Eqs. 10–13 in Part 1 (Thornton et al., 1985). The formulation and significance of these equations has already been discussed (*loc cit*) and will not be repeated here. The resulting histograms are shown in Figures 12 to 15 for the first, second, third and fourth disturbances.

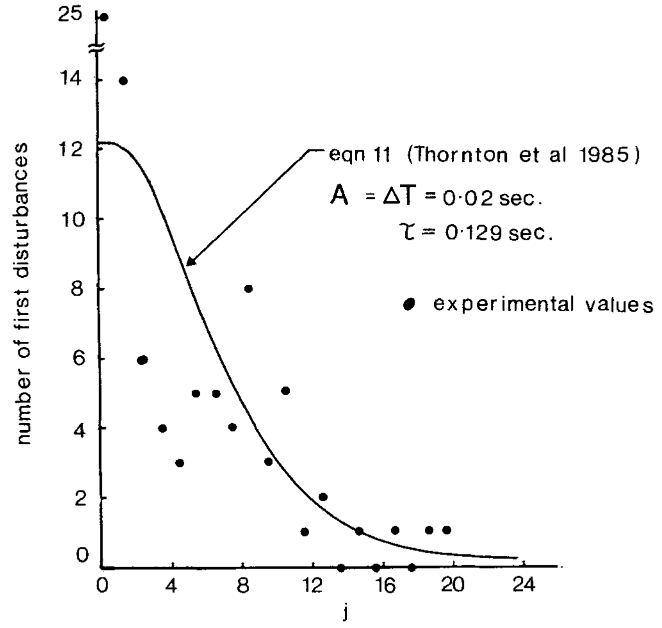

Figure 12. Histogram of first disturbances.

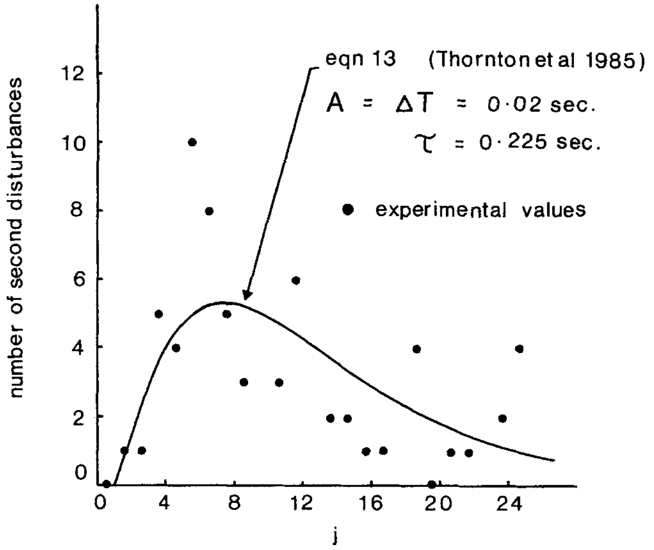

Figure 13. Histogram of second disturbances.

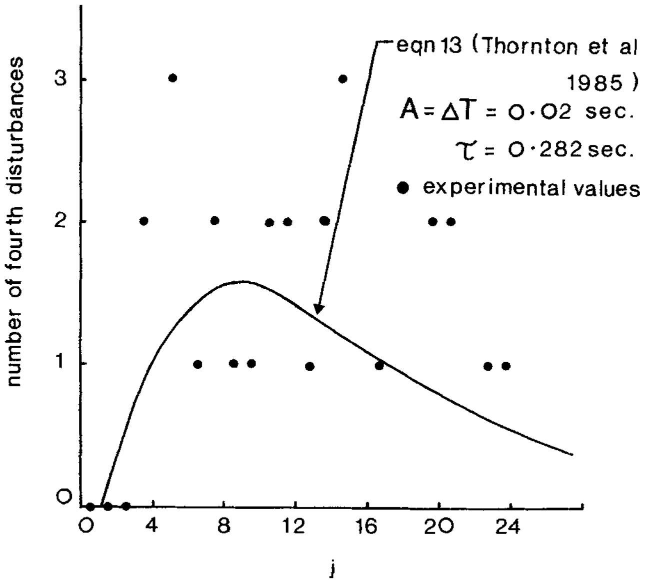

Figure 15. Histogram of fourth disturbances.

Discussion

Mass transfer

The results of the present investigation have shown that the overall mass transfer coefficient based upon the droplet phase is initially high but decreases with time and ultimately approaches a steady-state value. This behavior is common to all three solute concentrations used in this work, but the magnitude of the initial enhancement in the coefficient is noticeably higher at the higher solute concentrations. A qualitative confirmation of these two aspects is also evident in Figures 7 to 11. Thus, the tracer spot shows a faster dispersion at higher solute concentrations due to higher frequencies of the interfacial disturbances. Moreover, for a given solute concentration, a slower dispersion of the spot is shown at a higher age of the interface due to a decrease in frequency of the interfacial disturbances.

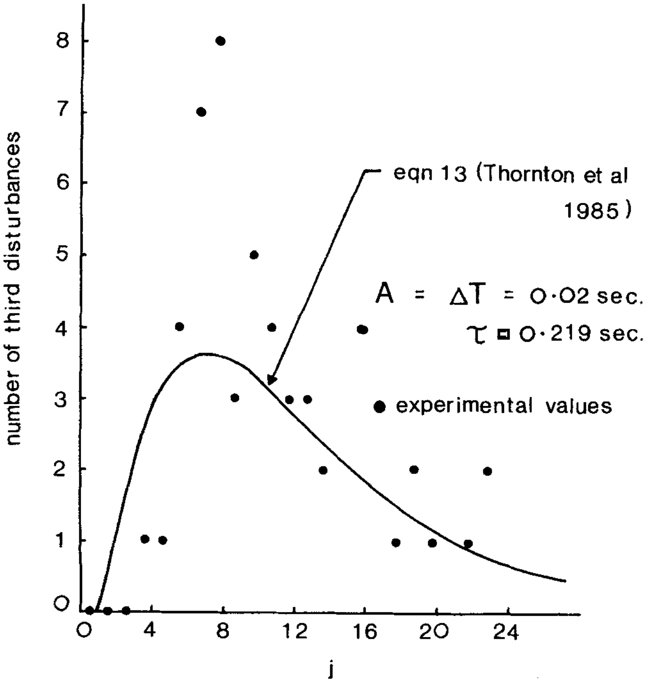

Figure 14. Histogram of third disturbances.

The enhancement in the frequency of interfacial disturbances and correspondingly in the coefficients with an increase in the solute concentration is readily understandable, since the higher solute concentrations produce larger interfacial tension gradients along the interface and thus bring about an increased influence of the Marangoni effect. On the other hand, the progressive decrease of the coefficients with time is not fully understood, and various explanations of this phenomenon have been advanced. Thus, Sawistowski and Goltz (1963) considered that the damping of surface renewal resulted from an increase in interfacial tension, when liquid eddies of the bulk phase arrive at the interface from within the droplet. This is not likely to be the case in the present work having regard to the time-scale and the fact that the interior of the droplet was in rapid circulation.

A second possible explanation (Ruckenstein, 1968) considers that, as time progresses, the liquid elements taking part in the surface renewal process become relatively more saturated so that interfacial turbulence becomes weaker. This explanation was followed up in a series of subsidiary runs, in which the continuous toluene phase was slowly circulated in order to eliminate the possibility of concentration gradients. This had no influence, however, on the progressive decrease of the coefficients with time.

A third possibility envisages a progressive accumulation of contaminants at the interface which suppress the interfacial activity and increase the interfacial viscosity. While this possibility is attractive, it is all too easy to attribute the present findings to this cause and further work is required in this area before the phenomenon is properly understood.

While the present study does not provide any explanation for the time dependence of the coefficients, it does nevertheless quantitatively confirm that surface renewal is the mechanism by which higher coefficients are produced in the presence of interfacial activity. It is interesting to note that similar time effects have been observed with inorganic solutes such as uranyl nitrate (Rogers et al., 1987).

In the absence of an explanation for the time dependence effect, the coefficient-time data have been treated empirically and have been found to exhibit an exponential relationship. The magnitude of the initial enhancement ($K_{od\max} - K_{ods}$) shows a dependence on the solute concentration in the organic phase. The corresponding values of the decay constant (m), however, decrease as the solute concentration increases, thereby implying slower rates of decay at higher solute concentrations. Javed and Thornton (1984) suggested that the progressive decay in the degree of enhancement of the transfer rate over the steady-state value could be described by the flow response curves for n perfectly mixed vessels in series where n varied between unity and infinity corresponding to high and very low solute concentrations, respectively. A fundamental explanation of this trend, however, must await a better understanding of the factors governing the properties of liquid-liquid interfaces.

The application of existing theoretical droplet models (e.g., Newman, 1931; Kronig and Brink, 1950; Handlos and Baron, 1957) to the present work has not been possible due to certain limitations. Thus, for example, these models consider diffusion into the droplet when the continuous-phase resistance is negligible. This assumption is not valid here since the toluene-water-acetone system has comparable resistances in both phases. Furthermore, the use of improved forms of these models (Elzinga and Banchero, 1959; Wellek and Skelland, 1965), which take a finite continuous-phase resistance into account, has not been possible because of the difficulty of predicting satisfactorily the value of the continuous-phase film coefficient under the present experimental conditions. A further difficulty lay in the fact that, in order to predict mass transfer coefficients, it is necessary to define the flow pattern inside the droplet; this would require a further study of the dynamics of the present system. This would be relevant particularly when considering the models for a fully-turbulent system such as that proposed by Handlos and Baron (1957) which expresses the coefficient in terms of the terminal velocity of the droplet.

Surface renewal

As pointed out earlier, the rate of dispersion of the tracer spot as shown by Figures 7 and 11 is an indication of the dependence of both the intensity and frequency of the disturbance on the solute concentration and the age of the interface. Accordingly, the life time of the tracer spot decreases at higher solute concentrations but, for a given concentration, increases with the age of the interface. The aging effect is also obvious from the measurement of the frequencies of the successive disturbances for the 5% concentration. These measurements show that the interval between the consecutive disturbances increases with the age of the interface. This is also evident in Figures 12 to 15 which present the frequency histograms for each of the disturbances which have been observed in the present work. Thus, most of the first disturbances occur within 0.02 second of the spot creation; whereas, in the case of second disturbances, no disturbance is observed before a minimum interval of 0.02 second from the onset of the first perturbation. The corresponding minimum time intervals for third and fourth disturbances are both 0.06 second.

It should be noted that in the absence of mass transfer (Figure 7), the tracer spot does not show any indication of being perturbed and thus tends to have an infinite life. This implies that surface renewal, due to hydrodynamic turbulence, does not occur in the absence of mass transfer under the present experimental conditions. The tracer spot does, however, show surface circulation towards the nozzle but with a superimposed tendency to move very slowly towards the apex of the droplet. This is probably due to the higher density of the colored complex, which is marginally higher than that of the dispersed aqueous phase. This behavior is in contrast to that of a growing pendant droplet reported earlier in Part 1 where surface circulation was apparent but gravitational effects were not observed. This may well be due to the time-dependent geometry and the different flow regime in the growing droplet. It is unlikely, however, that any small difference in densities between the colored complex and the aqueous phase would influence the observed surface renewal accompanying mass transfer, particularly at the higher solute concentrations where the disturbances to the tracer spot are rapid so that its life is correspondingly small.

Table 2 compares the experimental coefficients with those calculated from Eqs. 10 and 13 as well as from Higbie's Eq. 14 using the likelihood estimates of the mean residence time of the fluid elements at the droplet surface. This comparison shows a close agreement between the estimated and experimental values of the mass transfer coefficients, particularly in the cases of the coefficients calculated from Eqs. 10 and 14. Equation 13, however, tends to give consistently high values; this is not unexpected, since this expression assumes fresh surface at the end of each disturbance.

The agreement of the other two equations with the experimental values suggests that, while the model used in the present work is a good approximation to the mass transfer process, Higbie's equation can be employed equally satisfactorily to predict the coefficients provided that the actual mean residence times of the fluid elements at the droplet surface are used as the contact time in this relation.

Turning to the effect of the term A on the mass transfer coefficient, it can be seen that Eq. 13 is more sensitive to the value of A than are Eqs. 10 and 14. Both predict only a very slight change in the mass transfer coefficient over the range of A values used here. This is due to the fact that an increase in A results in a decrease in the mean residence time and a corresponding increase in the coefficient. The insensitivity of Eq. 10 to the value of A suggests that the age and the residence time distribution functions used to interpret the frequency of the interfacial disturbances can be fairly approximated by corresponding functions for two first-order processes in series.

It is important to remember that the estimated values of the mean residence times and the corresponding values of the transfer coefficients were determined when the droplet was labeled in the middle region. Such values have been shown to be position-dependent for growing pendant droplets (Thornton et al., 1985), and it might also be anticipated to be the case here. In such a situation, the renewal characteristics need to be monitored as a function of position around the droplet profile and any generalised model must take such variations into account.

If the time-dependent nature of the transfer process proves to be a characteristic feature of systems which exhibit interfacial turbulence, it will have important implications for contacting equipment in general. In order to maintain high transfer rates, it will be important to ensure that the liquid-liquid interface is being renewed continuously. This is conventionally brought about in contactors which promote a rapid coalescence/redispersion cycle such as mixer-settlers, and it is possible that, for this reason, units of this type will be suitable especially for use with systems which exhibit time-dependent characteristics.

Conclusions

Both the rate of surface renewal through interfacial turbulence and the mass transfer coefficient decrease progressively with time as the droplet interface ages. The initial value of the transfer coefficient increases with increasing solute concentration in the continuous phase and falls to a steady-state value in parallel with the frequency of interfacial perturbations.

Simultaneous measurements of the mass transfer coefficients and the frequencies of interfacial disturbances have shown quantitatively that surface renewal induced by the Marangoni effect is the mechanism responsible for the enhanced coefficients observed with this system. Such coefficients are greater than those expected from a purely molecular diffusional mode of transfer.

The Higbie equation may be used to predict mass transfer coefficients, provided that the time of contact in this relation is synonymous with the observed mean residence time of the fluid eddies at the droplet interface.

These findings are significant in the design of contactors since, in the presence of interfacial effects, high coefficients can be maintained only by ensuring that the droplet age distribution corresponds to that of young droplets. This requirement places a premium on mechanical contactors in which fresh interface is maintained through a rapid coalescence/redispersion cycle.

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Notation

A = minimum duration of a roll cell, s
A_d = droplet surface area, cm^2
c = solute concentration, gmol/L
c_o = bulk-phase solute concentration, gmol/L
c^* = equilibrium concentration, gmol/L
$\mathcal{D}$ = molecular diffusivity cm^2/s
F = dispersed-phase flow rate, L/s
H = distribution coefficient
j = integer 2, 3 . . .
k = film mass transfer coefficient, cm/s
k_c = continuous-phase film coefficient, cm/s
k_d = dispersed-phase film coefficient, cm/s
K_{od} = overall dispersed-phase coefficient, cm/s
$K_{od\max}$ = initial value of K_{od}, cm/s
K_{ods} = steady-state value of K_{od}, cm/s
m = decay constant in Eq. 3
N = instantaneous mass flux, gmol/cm$^2 \cdot$ s
$\bar{N}$ = average mass flux, gmol/cm$^2 \cdot$ s
t = time, s
Δt = arbitrary time interval, s
V_d = droplet volume, cm^3

Greek letters

θ = age, s
τ = reciprocal fractional rate of surface renewal, s
$\phi(\theta)$ = age frequency density function

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