Drop Coalescence Mass Transfer

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In recent years much attention has been given to studies of the mass transfer behavior of single liquid drops. The rationale for this emphasis is that the operating characteristics of equipment in which one liquid phase is dispersed in another should ultimately be determined by what happens to individual droplets. In many industrial operations the flow conditions are turbulent and drop shapes often deviate from spherical; in addition, individual drops may coalesce with other drops or break up into smaller ones. Most of the work on single drops, however, has been done under restricted conditions to eliminate the effects of drop interactions.

The lifetime of a drop is generally divided into four mass transfer regimes: the formation at a nozzle or an orifice, an acceleration period, rise or fall at the terminal velocity, and coalescence. The period of free fall has been the most extensively investigated [see for example the classic studies by Garner, et al. (1959) and by Handlos and Baron (1957)], but the formation process has also been the subject of a number of investigations, the most recent being that of Skelland and Minhas (1971). Frequently, both formation and coalescence are considered to be end effects and the mass transfer is evaluated indirectly by an extrapolation technique as discussed by Johnson and Hamielec (1960). The recent studies by Rajan and Heideger (1971) and Dubois (1970) have provided the first direct measurements of drop formation mass transfer but, to the knowledge of the authors, no studies have been made of the mass transfer which occurs during coalescence of a pair of drops and only the simple model proposed by Johnson and Hamielec exists even for the less complex case of drop coalescence on a planar interface.

It can be argued that, for many real situations, a drop is nearly depleted in solute by the time it leaves the system by coalescence with the phase boundary. From the mass transfer standpoint, therefore, the coalescence of drop pairs is a potentially more significant phenomenon since it can occur at an early stage of drop life. This problem has not been dealt with in the chemical engineering literature except for a theoretical treatment of the overall influence of drop interactions by Bayens and Laurence (1969). For steady state or batch stirred tanks, they concluded that coalescence and redispersion might substantially enhance mass transfer. In spray towers, however, interactions may not be as significant since the effects of drop growth and drop mixing are opposed and the frequency of drop interaction is low. No experimental evidence is available to substantiate these conclusions. The present paper is the first report of our experiments on the effect of coalescence on single drop mass transfer.

EXPERIMENT

Measurements of mass transfer were accomplished by means of the photographic technique described by Lode and Heideger (1970). Changes in drop volume with time were determined from ciné photographs and were then smoothed and converted into mass transfer rates with the aid of a CDC 6400 computer. Two identical drops were formed in parallel at the tips of 16 gauge hypodermic tubing and were released simultaneously when the tubing nozzles were abruptly pulled away from the drops. At the instant of release the drop surfaces were approximately 1 mm apart and the water flow through the photographic channel was adjusted to hold the drops nearly stationary. Solute transfer out of the organic drops promoted their coalescence as a result of interfacial tension effects, and in many cases this coalescence occurred between 0.5 and 2 seconds after drop release. The combined drop thus formed was photographed continuously for 20 seconds and then intermittently for the next 5 minutes. Drop diameters were measured on magnified film images with the Vanguard Motion Analyzer, and a least squares convolution technique was employed to smooth this raw data. Drop volumes and solute concentrations were calculated from the smoothed time dependence of the diameter and finally the mass transfer rate was evaluated from the first derivative.

The dispersed phase solvent was a mixture of toluene and carbon tetrachloride (72:28) with a density of 0.984 gm/cm^3 at 23°C. It was thus possible to balance the continuous phase (water) velocity against the terminal velocity of the drop and with minimum distortion retain the drop within the camera field of view. The transferring solute, acetic acid, had a very high distribution coefficient (35:1 to 75:1, depending on concentration) between water and the inert organic, and therefore the resistance to mass transfer was predominantly in the dispersed phase. It was assumed that the influence of coalescence-induced mixing would be much more obvious in such a system. The organic solutions had relatively high interfacial tensions against water (36 dynes/cm), even at high solute concentration (15 dynes/cm @ 5%, still 3 dynes/cm even at 25%), which suggests that the solubility of inert was minimal. This was verified by a material balance over the drop after all solute had been extracted; this calculation was used to guide the initial fit since diameter measurements of the distorted drop immediately following coalescence were not considered reliable.

RESULTS AND DISCUSSION

The time dependence of solute concentration following coalescence was calculated from the measured drop sizes and is shown in Figure 1 for three different initial concentrations. The data points shown are raw data; no computer smoothing has been done. However, each point is the average of the measurements made on ten successive frames (film speed 62 frames/sec.), plotted at the midpoint of that ten-frame time interval. The general shape of all three curves is the same: a very rapid, initial decrease in concentration representing extremely rapid mass transfer which slowly decays, a break or plateau in the curve during which no concentration change occurs, and a second rapid decrease which gradually levels out at long contact times. These changes are even more obvious if the slopes of the curves in Figure 1 are used to calculate the mass transfer rates (Figure 2). The initial very high rates decay to zero in 3 to 4 seconds after coalescence, remain zero briefly, abruptly increase to a significant rate again, and finally decay slowly.

A possible explanation for the observed behavior may be developed on the basis of the following description of the coalescence event. When coalescence occurs, the doublet formed pulsates for a fraction of a second between reproducible axisymmetric shapes which soon become regular oblate and prolate spheroids. The drop appears to be spherical in approximately one second; however, it may be assumed that vigorous mixing has been established by the violent initial behavior and that this mixing brings fresh fluid to the drop interface and also thins the external boundary layer. It is likely that this mixing disappears more slowly than the surface distortion because of the low dispersed phase viscosity (~ 0.7 cp) and it is postulated that the competing, more ordered circulation induced by shear cannot assert itself until this initial agitation dies away. Once the drop becomes quiet, shear-induced circulation *is* established and the *mass transfer rate jumps* sharply.

The above explanation seems more reasonable when the following observations are considered: Although the photographs taken in this study were not designed to detect circulation, refractive index patterns related to circulation are sometimes evident. It is strongly suggested by these patterns that the initial circulation following coalescence is random while that which occurs 5-6 seconds later (after the plateau) has an ordered, probably toroidal form. Rose and Kintner (1966) reported that large oscillating drops did not display the regular Hadamard-like circulation pattern; when the oscillations died out, however, circulation was restored. Although the factors which lead to oscillation in the present study are quite different, it seems reasonable to assume that a similar exclusion phenomenon occurs.

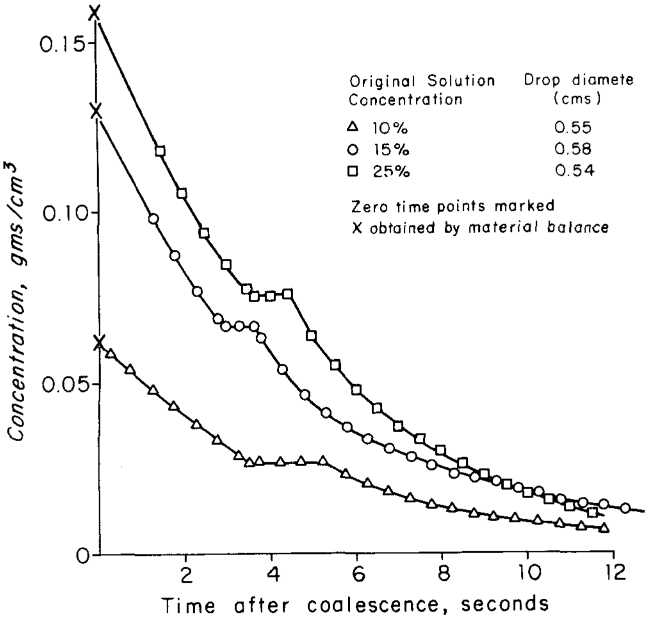

Fig. 1. Time dependence of solute concentration.

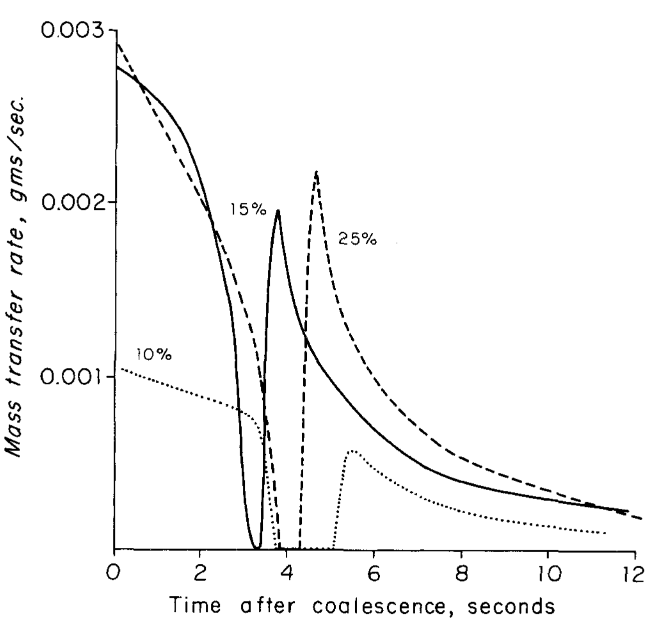

Fig. 2. The change in mass transfer rates as a function of time after coalescence.

Further confirmation of the proposed model may be obtained from an evaluation of terminal velocity effects. Small drops which have not coalesced exhibit shear-induced circulation, as evidenced by the considerable decrease in their terminal velocity when surfactant is added to damp out such circulation. The large drop formed by coalescence apparently does not undergo such ordered circulation since its terminal velocity is essentially the same as that of the small circulating drops from which it is formed. Since a larger drop generally circulates more readily, it would be expected to have a significantly higher velocity because of both size and circulation. The fact that it does not, plus the observation that its velocity increases after the first few seconds following coalescence, reinforces the argument that the initial mixing patterns must be random whereas the later ones appear to be ordered.

It does seem a little strange that there is no overlap of the two different modes of mixing. One might intuitively expect the shear-induced patterns to build up as the random motions decay to a low level. However, it is quite clear from both figures presented that a distinct period exists in all three cases considered during which no measurable mass transfer occurs. It is difficult to imagine such an event unless the drop actually comes to rest internally, at least in the vicinity of the interface, before the second circulation period begins.

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