Continuous-Phase Mass Transfer Coefficients for Liquid Extraction in Agitated Vessels: II

YOUNG I. MOK and ROBERT E. TREYBAL

Department of Chemical Engineering,
New York University, New York, New York 10453

In an earlier paper (*11*), the continuous-phase mass transfer coefficients resulting from the continuous-flow contact of ethyl acetate and water in an agitated vessel, ethyl acetate dispersed, were reported to be substantially larger than might be expected from consideration of the data obtained from solid particles in agitated liquids. The enhancement of the mass transfer coefficients was attributed to coalescence and redispersion of the drops of ethyl acetate as they were thrown radially from the impeller and circulated to the top and bottom of the vessel, eventually around again to the impeller. It was reasoned that coalescence and redispersion, both fairly violent processes, interfered with and destroyed the buildup of a steady state concentration gradient in the liquid surrounding the drops, and it was shown mathematically that this could substantially increase the time-average coefficients. For baffled vessels it was found possible to describe these coefficients reasonably well by the expression

$$k_C = k_s + 3.94(D_A/\theta_C)^{0.5} \qquad (1)$$

where k_s, a steady state coefficient, was estimated from the data for suspended solid particles of the same size as the drops (*2*), and θ_C represents the time between coalescences and redispersions. The latter was estimated for lack of a better means from observation of the change in mean drop size from the level in the vessel just opposite the impeller to that at the top and bottom:

$$\frac{1}{\theta_C} = 2\left[\frac{(d_{pT}^3 + d_{pB}^3)/2 - d_{pM}^3}{d_{pM}^3}\right]\frac{1}{t_C} \qquad (2)$$

The circulation time was estimated for the baffled vessels from the work of Holmes (*3*). The second term on the right of Equation (1) represents the enhancement of the mass transfer rate resulting from the relatively violent coalescence phenomenon; the constant 3.94 is empirical, chosen to fit the data best. The coefficients for the vessel without baffles, operated without an air-liquid interface and therefore without a vortex, were appreciably larger at the same impeller power, but lack of information on the circulation times in such vessels prevented inclusion of these data in the correlation represented by Equation (1).

CHOICE OF A NEW SYSTEM

It was considered very desirable to provide a further test of Equation (1), indeed to confirm even the necessity of the coalescence term, by making measurements with another liquid-liquid system. As described in the earlier paper, the technique of using two-component systems to confine the mass transfer to the continuous phase severely limits the number of liquids from which a choice may be made, particularly in view of the cost. Among those which might be useful, there is relatively little percentage change in the diffusivity in water as compared with that for ethyl acetate. Consequently it was thought that by using a liquid which would provide a substantially smaller density difference between the drops and the continuous phase, a significant difference in the coalescence frequency would result, thus providing a good test of the coalescence term of Equation (1). This proved to be the case. The work described in this paper was done with paraldehyde saturated with water as the dispersed phase, with water continuous, a system which provides a density difference between the mutually saturated liquids of 0.013 g./ml. at 20°C., as contrasted with 0.089 g./ml. for ethyl acetate-water. The paraldehyde assayed 99.9% by weight, with refractive index at 20°C. = 1.4049; the diffusivity in water at 25°C. = 3.25 (10^{-5}) sq.ft./hr., and the interfacial tension of the mutually saturated liquids = 6.96 dynes/cm. [for ethyl acetate-water, the diffusivity = 3.4 (10^{-5}) sq.ft./hr.; interfacial tension = 6.4 dynes/cm.]. At 25°C. the mutually saturated liquids contain 10.09 and 99.81 wt. % aldehyde, respectively.

EQUIPMENT

The same apparatus and procedures with only minor modifications were used as in the previous study (*11*). The glass mixing vessel—9.5 in. I.D., 9.5 in. tall, with stainless steel closures—was agitated with centrally located six-blade, flat-blade turbine impellers, 5-in. diam. for the vessel fitted with four 10% wall baffles, 3-in. diam. for the unbaffled vessel. The vessel was operated full of liquid at all times, without an air-liquid interface, hence without vortex. During mass transfer measurements impeller speeds ranged from 100 to 500 r.p.m., total flow rate 1,035 to 1,750 lb./hr., and dispersed-phase holdup in the vessel 0.5 to 9.9%.

As before, the specific interfacial area was determined by a light-transmittance technique with an arrangement to traverse the vessel vertically with the glass rods used to conduct the light (*11*). The rods, silvered instead of platinized, were encased in stainless steel tubing for protection. The light-transmittance device was calibrated by placing the gap between the rods at the bottom of the vessel, photographing the dispersion

---

Correspondence concerning this article should be addressed to Prof. R. E. Treybal. Young I. Mok is with E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898.

through a glass window in the base of the vessel, and sampling the liquid locally to obtain the phase ratio. The photographs provided the average drop diameter, which, together with the phase ratio, permits calculation of the specific interfacial area and calibration of the light-transmittance assembly. Phase ratio was determined by withdrawing a much larger sample (ca. 250 ml.) of the vessel contents than in the previous study, with the result that the phase ratio data upon which drop diameter and interfacial surface estimates are based, are believed to be substantially more accurate than before. During the mass transfer runs, these samples were taken at positions 0.33, 4.5, and 8.0 in. from the bottom of the vessel. Samples of the continuous phase free of paraldehyde drops, for analysis, were taken from the vessel by withdrawing them through a fritted glass filter of medium porosity, average pore opening 15 μ. The aqueous solution was analyzed with a Bausch and Lomb precision refractometer. Continuous-phase mass transfer coefficients and mean specific areas were computed in the same manner as in the previous work. Further details are available (*10*).

SPECIFIC AREA AND DROP SIZE

Figure 1 shows typically how the light-transmittance data varied with height in the vessel. Since the dispersed-phase holdup was locally largest at the center, the specific interfacial area similarly passed through a maximum and the drop size through a minimum at the position opposite the impeller. Mean specific interfacial areas for the entire vessel as a whole are shown in Figures 2 and 3 for the baffled and unbaffled vessels, and the corresponding mean drop sizes are in Figures 4 and 5. Neither the mean specific area nor the mean drop size is materially influenced by flow rate, at least over the range of rates studied. All these observations are qualitatively very similar to those made with ethyl acetate-water (*11*), although drop sizes in the latter were generally smaller.

CIRCULATION IN THE UNBAFFLED VESSEL

Average circulation times needed for Equation (2) are available for baffled vessels from the work of Holmes (*3*), but none were known for unbaffled vessels. Accordingly these were determined by placing a 0.5-g. polyethylene particle, made neutrally bouyant by embedding in it short pieces of fine copper wire, in the vessel filled with water. The vessel was imagined to be divided into five horizontal zones indicated by markings on the outside of the glass: zone 1 at the bottom, 3 at the impeller level, and 5 at the top. The time required for the particle to travel from zone 3 to zone 5 (or to zone 1) and back to zone 3 was then considered the circulation time. For each impeller speed and flow rate, the zone where the particle was located at particular times was recorded verbally on a tape recorder for 2 hr. These several hundred observations then produced one average circulation time. The data are shown in Figure 6.

COALESCENCE FREQUENCY

For the data taken during mass transfer measurements, the coalescence-redispersion frequencies were computed by means of Equation (2), and are shown in Figures 7 and 8. Since only the overall change in drop size between the impeller level and the top or bottom of the vessel was known, it cannot be overemphasized that these can only be considered to be the bare minimum values of the frequency. As observed in earlier work (*8, 11*), impeller speed has a strong influence on the frequency, but the influence of increased dispersed-phase holdup is small, unlike the experiences with ethyl acetate-water. In addition, the frequencies are substantially lower than those observed with ethyl acetate-water.

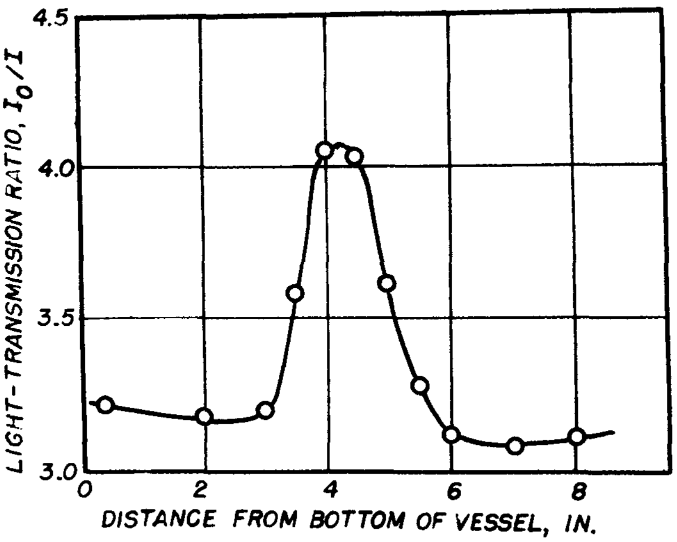

Fig. 1. Typical light probe traverse, baffled vessel, 5-in. turbine, average $\varphi_D = 0.01732$, total flow = 1,170 lb./hr.

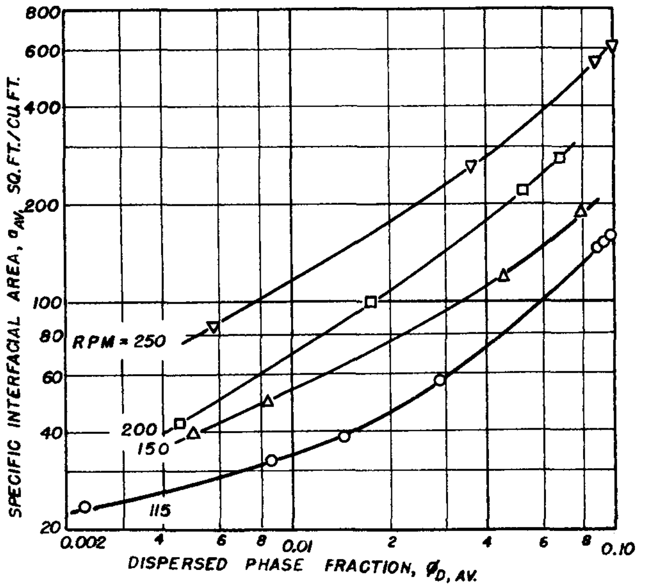

Fig. 2. Mean specific interfacial area, baffled vessel, 5-in. turbine.

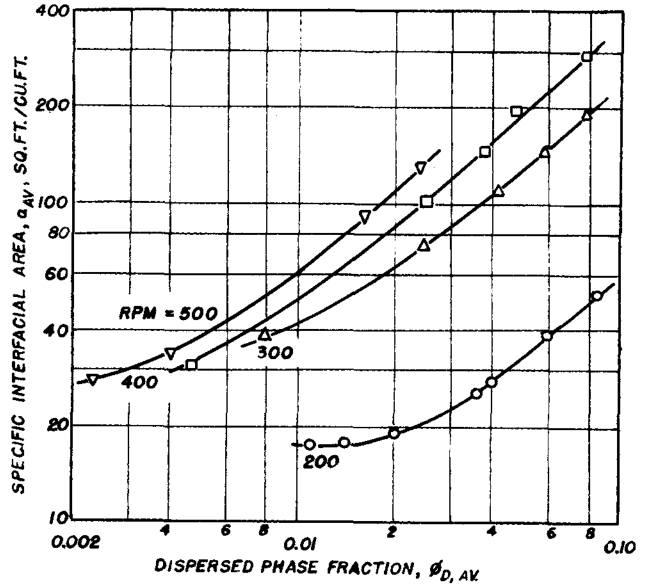

Fig. 3. Mean specific interfacial area, unbaffled vessel, 3-in. turbine.

That the differences in coalescence rate might be due to the presence of unsuspected minute amounts of a surface-active contaminant in the paraldehyde was a possibility, since such contaminants severely reduce coalescence rates (*9*). Garner and Skelland (*1*) had noted that these contaminants can result in a marked decrease in the terminal settling velocity of single liquid drops; consequently these were measured for paraldehyde drops in water, both phases mutually saturated, in a 3-in. diam., 6-ft. long glass cylinder. For drops of diameter 0.00128 to 0.0224 ft., which are below the transition size, the terminal velocities agreed excellently with the standard values (*6*, *7*), so surface-active contaminants were probably not present. It is believed instead that coalescence differences for paraldehyde-water and ethyl acetate-water are due to the small density difference between the drops and the continuous phase in the case of the former, and this was the reason for choosing this liquid pair. The drops are then more likely to follow closely the fluid motion and retain their relative distances, thus offering less opportunity for collision, than with the larger density difference of ethyl acetate-water.

An observation worthy of note was made during the terminal velocity measurements. If two drops ascended in line, the following drop was sucked into the wake of the leading drop and the two coalesced upon collision. Drops which were not in line, colliding with a glancing blow, tended to bounce apart and not to coalesce. This may explain the success of the analysis of coalescing drops based on head-on collisions offered elsewhere (*9*). When coalescence did occur, it was extremely rapid and violent. The resulting large drop momentarily stopped its ascent and vibrated or shuddered for a short time before resuming its rise. This tends to confirm the basis for Equation (1).

A rapid decrease in turbulence intensity can be expected to favor coalescence (*4*). When fluid is thrown radially from the impeller toward the vessel wall, the reduction in turbulence intensity which it experiences can be expected to be greater for the unbaffled vessel than for the baffled. Thus at an impeller power of some 3,500 (ft.)(lb.)/hr., with dispersed-phase holdup of 3%, each drop experiences at least 20 and 7 coalescence-redispersions per minute in the unbaffled and baffled vessels, respectively.

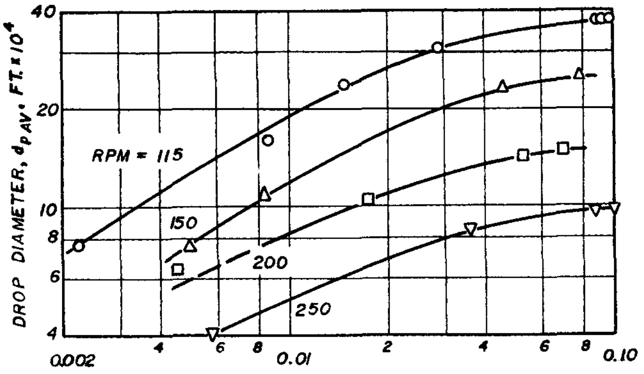

Fig. 4. Mean drop diameter, baffled vessel, 5-in. turbine.

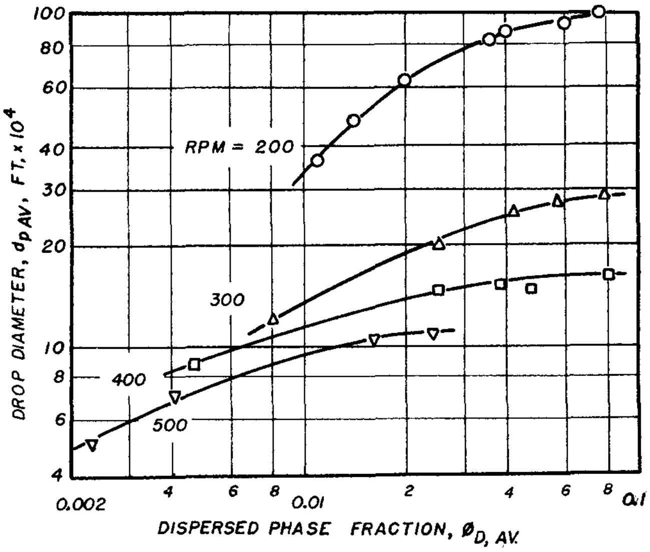

Fig. 5. Mean drop diameter, unbaffled vessel, 3-in. turbine.

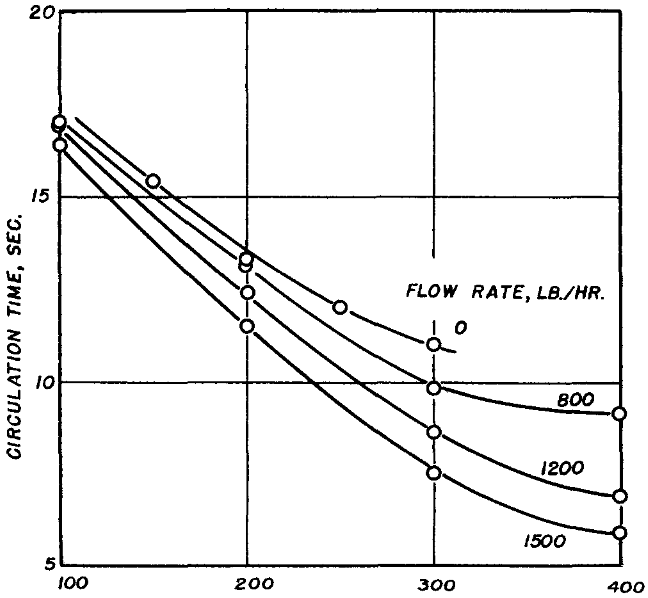

Fig. 6. Circulation times, unbaffled vessel, 3-in. turbine.

MASS TRANSFER COEFFICIENTS

If the mass transfer coefficients are plotted simply against impeller Reynolds number for all the data, a general increase of k_C with Reynolds number may be noted, but the influence of other variables is sufficiently strong that few conclusions can be drawn. It is clear, however, that k_C is larger (from 12.6 to 60.9%) than for comparable suspended solids. Furthermore, k_C is approximately twice as large, and k_Ca approximately five times as large, for the unbaffled vessel as for the baffled vessel at the same impeller power. The explanation is believed to be the greater coalescence frequency in the unbaffled vessel.

It has been suggested that the increase in k_C over that expected for solids might be attributable to circulation within the droplets. There is no information on drop circulation for swarms of drops, but Hughmark (*5*) has suggested, for μ_C/μ_D less than unity (it is 0.74 in the present case), that k_C for single drops and noncoalescing swarms are the same. Perhaps, then, we may reason from the data for single drops. The data of Thorsen and Terjesen (*13*) show divergence of k_C from that of solid spheres at values of $N_{Re}^{1/2} N_{Sc}^{1/3}$ of about 75. Since in this case N_{Sc} is 1,170, then the divergence would presumably begin at

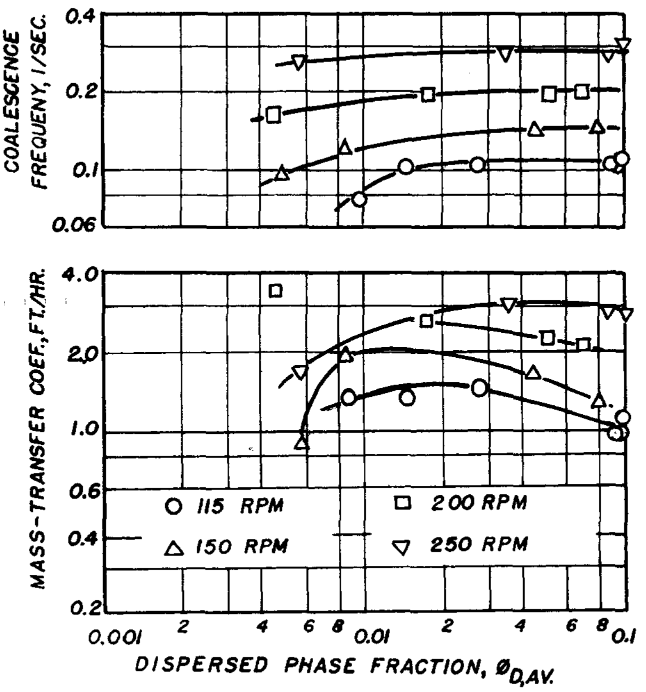

Fig. 7. Minimum coalescence frequencies and mass transfer coefficients, baffled vessel, 5-in. turbine.

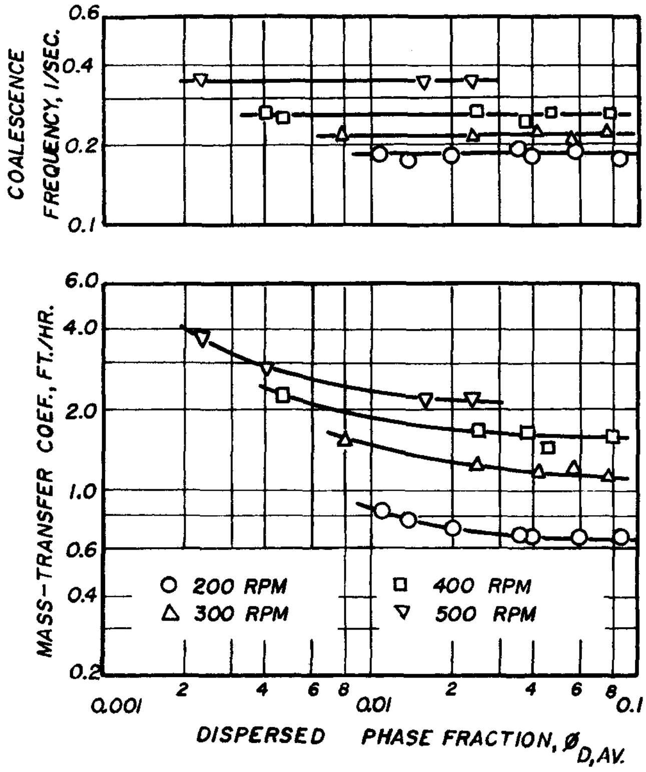

Fig. 8. Minimum coalescence frequencies and mass transfer coefficients, unbaffled vessel, 3-in. turbine.

$N_{Re} = 38$. If N_{Re} for the drops is computed with their terminal velocity, only the four largest drops of Figure 5 produce Reynolds numbers this large. Hughmark (*5*) has correlated the data for single drops, permitting estimates of the ratio of k_C for circulating and rigid spheres, k_{Cc}/k_{Cr}, if the particle slip velocity can be estimated. Schwartzberg's estimate of slip velocity of particles in baffled vessels (*12*) is for solids, but it shows the slip velocity to be substantially smaller than the terminal settling velocity. It cannot be applied to unbaffled vessels, however. Consequently the ratio of coefficients was calculated using the drop terminal settling velocities, which would predict more circulation than actually occurred. For the baffled vessel, k_{Cc}/k_{Cr} averages 1.14, with values of essentially unity for most runs, whereas $k_{C\text{obs}}/k_{Cr}$ averages 1.62. For the unbaffled vessel, k_{Cc}/k_{Cr} approaches the observed ratio only for the four largest drops of Figure 5. The rest average 1.035, whereas $k_{C\text{obs}}/k_{Cr}$ averages 1.39. Circulation evidently is small for the small drops encountered here, yet the mass transfer coefficients are substantially enhanced over those for solids. Furthermore, within-drop circulation cannot account for the variation of k_C with φ_D observed in the present and in the earlier work (*11*). We believe that drop coalescence and redispersion can.

The data for k_C are shown in Figures 7 and 8, where the effects of the influencing variables become clear. For suspended solids of the size of the paraldehyde drops, Harriott (*2*) shows that the mass transfer coefficient decreases with increased particle diameter. Since, as dispersed-phase fraction φ_D increases and the drop size increases (Figures 4 and 5), one might expect the k_C's of Figures 7 and 8 to decrease continually with increased φ_D. However, in the case of the baffled vessel, Figure 7, the initial rise in coalescence frequency with increased φ_D exerts a stronger influence and k_C initially rises. When the coalescence frequency ultimately levels off with increased φ_D, k_C similarly levels off and eventually decreases. In the case of the unbaffled vessel, with coalescence frequency constant with increased φ_D, the decreasing values of k_C reflect the continued corresponding increase in drop size. All the k_C's, however, are larger than those for solids.

Both sets of data were fitted to equations of the form of Equation (1); values of k_s were computed from the data of Harriott (*2*) for solid particles, since they include particle sizes corresponding to the paraldehyde drops, and coefficients for the transient, coalescence term determined to fit the data. The constants were 4.38 for the baffled vessel and 3.05 for the unbaffled. These are sufficiently close to

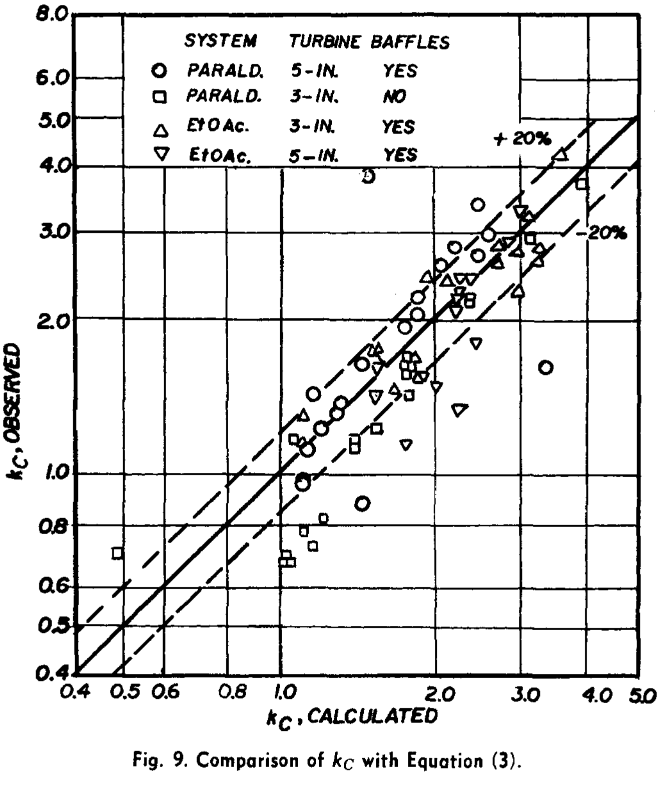

Fig. 9. Comparison of k_C with Equation (3).

the 3.94 obtained for the ethyl acetate-water system, considering the accuracy of the measurements, that rounding them all off to 3.9 seems most reasonable:

$$k_C = k_s + 3.9\ (D_A/\theta_C)^{0.5} \qquad (3)$$

Figure 9 shows the comparison of the new data as well as the earlier data (*11*) from baffled vessels with those computed from Equation (3). It is not now possible to recover the information needed to include the earlier data from unbaffled vessels, unfortunately. Most of the data are represented by Equation (3) within 20%. Considering the great number of measurements represented by each plotted point, the scatter is not considered excessive, and the applicability of the proposed mechanism seems reasonably well confirmed. More reliable coalescence data are obviously urgently needed.

ACKNOWLEDGMENT

This work was done under Grant G-21526 of the National Science Foundation, whose support is most gratefully acknowledged.

NOTATION

a = specific interfacial area, sq.ft./cu.ft.
d_p = drop diameter, ft.
D_A = diffusivity of the solute, sq.ft./hr.
I_0/I = incident light intensity/emergent light intensity
k_C = time-average continuous-phase mass transfer coefficient, lb.-moles/hr. (sq.ft.) (lb.-moles/cu.ft.)
k_s = steady state continuous-phase mass transfer coefficient, lb.-moles/hr. (sq.ft.) (lb.-moles/cu.ft.)
N_{Re} = drop Reynolds number
N_{Sc} = continuous-phase Schmidt number
t_C = circulation time, hr.
θ_C = time between coalescences, hr.
μ_C = continuous phase viscosity, lb./(ft.)(hr.)
μ_D = dispersed phase viscosity, lb./(ft.)(hr.)
φ_D = volume fraction dispersed phase

Subscripts

av = for the vessel as a whole
B = bottom of the vessel
c = circulating sphere
M = middle of the vessel
obs = observed
r = rigid sphere
T = top of the vessel

LITERATURE CITED

1. Garner, F. H., and A. H. P. Skelland, *Chem. Eng. Sci.*, **4**, 149 (1955).
2. Harriott, P., *AIChE J.*, **8**, 93 (1962).
3. Holmes, D. B., R. M. Voncken, and J. A. Dekker, *Chem. Eng. Sci.*, **19**, 201 (1964).
4. Howarth, W. J., *AIChE J.*, **13**, 1007 (1967).
5. Hughmark, G. A., *Ind. Eng. Chem. Fundamentals*, **6**, 408 (1967).
6. Hu, S., and R. C. Kintner, *AIChE J.*, **1**, 42 (1955).
7. Klee, A. J., and R. E. Treybal, *ibid.*, **2**, 444 (1956).
8. Madden, A. J., and G. L. Damerell, *ibid.*, **8**, 233 (1962).
9. Maraschino, M. J., and R. E. Treybal, *ibid.*, in press.
10. Mok, Y. I., Ph. D. dissertation, New York Univ., New York (1969).
11. Schindler, H. D., and R. E. Treybal, *AIChE J.*, **14**, 790 (1968).
12. Scwartzberg, H. G., and R. E. Treybal, *Ind. Eng. Chem. Fundamentals*, **7**, 6 (1968).
13. Thorsen, G., and S. G. Terjesen, *Chem. Eng. Sci.*, **17**, 137 (1962).

Manuscript received February 9, 1970; revision received May 4, 1970; paper accepted May 7, 1970. Paper presented at AIChE Atlanta meeting.

Dispersion in Laminar Flowing Liquid Films Involving Heat Transfer and Interfacial Shear

F. H. SHAIR

Department of Chemical Engineering,
California Institute of Technology, Pasadena, California 91109

Chemical reactors utilizing downward flowing liquid films have certain advantages when the reaction temperature must be carefully controlled (*1*). When the reaction is highly exothermic, the wall is cooled and the film is kept thin. Generally, the gas-phase reactant is diluted, and the flows are concurrent to avoid flooding. Chien (*2*) has correlated the static pressure gradient and superficial friction factor with the superficial gas and liquid Reynolds numbers. Stainthorp and Batt (*21*) have investigated the wave properties in a downward concurrent two-phase system. Although many investigations have been performed with falling films (for example see references *4* to *6*), much less

---

Correspondence concerning this article should be addressed to Prof. F. H. Shair.