

- Δn_2 = Differential analysis of compression-permeability tests n_1 and n_2 [Compare Equation (9)].
- g_c = Newton's gravitational constant 32.1740, (lb. mass)(ft.)(lb. force) (sec.²)
- k = numerical constant
- K = parabolic parameter, sec. or min./sq. ft.
- m = ratio of mass of wet cake to dry cake
- μ = filtrate viscosity, lb.-mass/(ft.)(sec.)
- P = filtration pressure, lb.-force/sq. ft.
- P_z = hydrostatic pressure at any point lb.-force/sq. in.
- P_m = mechanical pressure on cake particles or solids, lb.-force/sq. in.
- ρ = filtrate density lb.-mass/cu. ft.
- R_c = resistance of cake solids to fluid flow, 1/ft.
- R_d = resistance of filtration deposition zone to fluid flow, 1/ft.
- R = resistance of equipment leads, fittings, etc. to fluid flow, 1/ft.
- R_m = resistance of filter cloth or septum to fluid flow, 1/ft.
- s = prefill consistency, weight of oven-dry solids to prefill weight
- θ = filtration time, hr.
- θ_m = time equivalent of V_m , hr.
- $\frac{d\theta}{dV}$ = filtration rate, hr./cu. ft.
- $\frac{\Delta\theta}{\Delta V}$ = filtration rate calculated as $(\theta_{n+1} - \theta_n)/\frac{1}{2}(V_{n+1} + V_n)$ when successive values of $V_{n+1} - V_n$ are equal, hr./cu. ft.
- V = fluid or filtrate volume, cu. ft.
- V_m = filtrate volume equivalent to filter cloth resistance, cu. ft.
- $\frac{dV}{d\theta}$ = fluid or filtrate rate, cu. ft./hr.
- w_c = oven-dry weight of cake solids deposited per cubic foot of filtrate discharged, lb.
- W_c = oven-dry weight of cake solids, lb.
- W_m = oven-dry weight of cake solids equivalent of R_m , lb.
- $W_t = W_c + W_m$, lb.

LITERATURE CITED

1. Carman, P. C., *Trans. Inst. Chem. Engrs. (London)*, **15**, 150 (1937).
2. *Ibid.*, **16**, 168 (1938).
3. Ergun, S. K., *Chem. Eng. Progr.*, **48**, 89 (1952).

4. Fair, G. M., and L. P. Hatch, *J. Am. Water Works Assoc.*, **25**, 1151 (1933).
5. Grace, H. P., *Chem. Eng. Progr.*, **49**, 303 (1953).
6. *Ibid.*, p. 367.
7. *Ibid.*, p. 427.
8. Hatschek, Emil, *J. Soc. Chem. Ind. (London)*, **27**, 538 (1908).
9. Hawksley, P. G. W., "The Effect of Concentration on the Settling of Suspensions and Flow Through Porous Media," pp. 114-135, Edward Arnold and Co. London, (1951).
10. Hoffing, E. H., and F. J. Lockhart, *Chem. Eng. Progr.*, **47**, 3 (1951).
11. Kottwitz, F. A., unpublished Ph.D. thesis, Iowa State Coll., Ames (1955).
12. Kozeny, Joseph, *Sitzber. Akad. Wiss. Wien., Math. naturw. Kl. Abt. IIa*, **136**, 271 (1927).
13. Ruth, B. F., *Ind. Eng. Chem.*, **38**, 564 (1946).
14. Ruth, B. F., *Ind. Eng. Chem.*, **27**, 708 (1935).
15. Ruth, B. F., unpublished Ph.D. thesis, Univ. Minn., Minneapolis (1931).
16. ———, G. H. Montillion, and R. E. Montonna, *Ind. Eng. Chem.*, **25**, 153 (1933).
17. Sullivan, R. R., *J. Appl. Phys.*, **12**, 503 (1941).
18. Tiller, F. M., *Chem. Eng. Progr.*, **49**, 467 (1953).
19. *Ibid.*, **51**, 282 (1955).

Individual Film Coefficients of Mass Transfer in Liquid-liquid Extraction

G. C. SMITH and R. B. BECKMANN

Carnegie Institute of Technology, Pittsburgh, Pennsylvania

A study has been made of the individual film coefficients of mass transfer for two binary liquid-liquid systems of differing physical properties, namely methyl isobutyl carbinol-water and methylethyl ketone-water, in a 4-in. diam. extraction column operated as a spray column and with 1/2-in. Raschig ring packing. The value of H_i for the dispersed phase was found to be a constant, C_1 , for a given system in a given column. The H_i values for the continuous phase could be correlated by the equation,

$$(H_i)_c = C_2(V_c/V_d)^n$$

Values of the constants C_1 , C_2 , and n are tabulated along with the values found by earlier investigators for other systems and column packings. The H_i values have been reduced to area base coefficients by the expression for droplet surface area proposed by Gaylor and Pratt (3).

Presaturation of either phase was found to have no effect on mass transfer rates. There appears to be relatively little difference in the efficiency of spray and packed columns for systems of low interfacial tension, but for high interfacial-tension systems packed columns are considerably more efficient than spray columns.

While no definitive correlations for the effect of physical properties are proposed, there are some indications that n is a function of the viscosity ratio of the two liquid phases and that C_2 is a function of the 1/4 power of the groups $(d\Delta\rho\gamma/\mu^2)(\mu_c/\mu_d)$ and $(N_{Sc})_c$. No correlation was found for the effect of physical properties on $(H_i)_d$.

In recent years the unit operation of liquid-liquid extraction has assumed an

increasing importance as the separation problems of modern process chemistry have become more complex. While many new forms of extraction equipment have been proposed recently, particularly those involving mechanical agitation to improve the two-phase contact, the

packed column remains one of the simplest and most economical extractors to build and operate. Such columns are easily and cheaply assembled from stock parts and are generally less expensive to operate than rotating disk contactors, pulsed columns, centrifugal extractors,

This paper is based on a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Carnegie Institute of Technology.

G. C. Smith is presently with E. I. duPont de Nemours & Company, Wilmington, Delaware.

or other devices involving mechanical agitation or separation of the phases.

Two main considerations govern the selection of the diameter and height of column and the size and type of packing. These are the limiting liquid velocities and the rate of mass transfer. The limiting flow rates have been investigated extensively and can be predicted with some confidence. The investigation of mass transfer rates presents a much more complicated problem, and although many investigations have been carried out, there are many questions which remain unanswered. A complete picture of mass transfer processes would include accurate knowledge of the holdup of the dispersed phase and the average droplet size and shape, by which the surface area available to mass transfer could be predicted, and a knowledge of the fundamental single film coefficients of mass transfer on an area basis.

The holdup problem has received considerable attention in recent years (5, 15, 18) and appears to be a complex phenomenon. As yet, no reliable generalized correlations are available for prediction of holdup. The problem of droplet size and shape has received some attention (3, 8, 14), but the methods employed can be regarded only as yielding approximate results. A considerable number of studies have been made on the mechanism of mass transfer across a liquid-liquid interface (7, 9, 13, 17), and here, too, the theoretical picture is far from complete. It appears that many years of effort will be required to complete this fundamental picture of extraction-column operation.

A simpler measure of mass transfer rates which can yield results of immediate usefulness to the design engineer is the capacity coefficient in terms of ka or H_i values. These are generally measured as over-all coefficients for the transfer of a solute from one phase to another. These over-all coefficients can be broken down into individual coefficients only when severe restrictions are applied concerning the nature of the individual coefficients.

To avoid this difficulty, Colburn and Welsh (2) devised a method of determining the individual coefficients directly in an extraction column by contacting two partially miscible liquids with no distributed third solute present. This is analogous to contacting a pure gas and a pure liquid in an absorption column. If the two-film theory is applied to such a system, it is found that the assumption of equilibrium at the interface implies that immediately adjacent to the interface each phase is saturated with the material of the opposite phase, or $y_i = y^*$. At constant temperature, y^* , the saturation concentration of the materials of the opposite phase in the phase under consideration, will be constant and the equation for number of transfer units may be integrated directly. The number of

transfer units thus obtained is the individual number of transfer units for the phase under consideration.

$$N_i = \int_{y_1}^{y_2} \frac{dy}{y^* - y} = \ln \frac{y^* - y_1}{y^* - y_2} \quad (1)$$

Binary systems of partially miscible liquids have been used in several investigations of the individual film coefficients of mass transfer. Gordon and Sherwood (7) and Lewis (13) determined coefficients on an area basis in nonflow systems of known interfacial area. Murphy, Lastovica, and Skrzec (16) employed a horizontal tube extractor to measure area-based coefficients for two liquid phases flowing countercurrent to each other. An interface of known dimensions was maintained along the center line of the tube with the light liquid occupying the upper half and the heavy liquid the lower half of the tube. Correlations, relating the coefficients to the physical properties and Reynolds numbers of the flowing phases, were presented.

In the first investigation employing binary liquid-liquid systems, Colburn and Welsh (2) measured mass transfer rates for the system isobutanol-water in a packed column. Their results were correlated by the following equations:

$$(H_i)_d = C_1 \quad (2)$$

$$(H_i)_c = C_2 \left(\frac{V_c}{V_d} \right)^n \quad (3)$$

Laddha and Smith (11) employed the systems isobutyraldehyde-water and 3-pentanol-water in a packed column and a spray column. They were able to correlate their results with the above equations with the use of different values for the constants. Attempts to correlate the results with system physical properties were largely inconclusive. Gaylor and Pratt (4) measured individual coefficients with the system ethyl acetate-water in a packed column. Holdup data were taken in order to reduce the coefficients to an area basis by use of Equation (4)

$$a = \frac{6\epsilon x'}{d_{vs}} \quad (4)$$

End effects were also measured by varying the packed height. These last three papers are discussed in more detail where they are compared with the results of the present study.

Ruby and Elgin (17) measured the rates of mass transfer into the continuous phase for five different systems in a spray column, and Heertjes, Holve, and Talsma (9) used a similar technique to measure mass transfer into a continuous water phase from a dispersed isobutanol

TABLE 1.
EQUILIBRIUM DATA

Mutual solubility Temp. (°C.)	M.I.B.C.-water	
	wt. % water in M.I.B.C.	wt. % M.I.B.C. in water
0.0	5.48	—
10.0	5.78	2.27
15.0	5.96	2.05
20.0	6.15	1.87
25.0	6.35	1.72
30.0	6.58	1.59
35.0	6.89	1.47
40.0	7.20	1.37

Mutual solubility Temp. (°C.)	M.E.K.-water	
	wt. % water in M.E.K.	wt. % M.E.K. in water
20.0	11.59	27.33
25.0	11.72	25.57
30.0	11.85	24.07

phase in a spray column. Their columns were greatly simplified in order to count droplets and a special sampling technique was employed to eliminate end effects. Because of the specialized nature of the measurements, the last two papers were not considered suitable for comparison with the present study.

SCOPE OF INVESTIGATION

The purpose of the present investigation was to measure the individual coefficients of mass transfer for two binary systems of differing physical properties. Physical properties for the two systems, methyl isobutyl carbinol (M.I.B.C.)-water and methyl ethyl ketone (M.E.K.)-water, are given in Table 6. A 4-in. extraction column was used for all experiments and measurements were made on each system in spray, or unpacked, column operation and with 1/2-in. Raschig ring packing. Each system was also run in three different ways in each type of column. Initially, runs were made with two pure liquid phases in contact so that simultaneous counterdiffusion of each phase into the opposite phase occurred; second, runs were made with one phase presaturated with the opposite phase so that unidirectional diffusion into the unsaturated phase occurred; and finally, runs were made with the other phase presaturated, which gave unidirectional diffusion in the opposite direction. In all runs, water was the continuous phase and the organic liquids were introduced at the bottom of the column as the dispersed phase.

The mass transfer results for a given liquid-liquid system in a given column were correlated with flow rates by Equations (2) and (3). These correlations were then compared to assess the effects of

presaturation and of packed and spray column operation for each system. Finally, the correlations obtained in this investigation were compared with those obtained by earlier investigators on other binary systems in an attempt to determine the effect of system physical properties on the rates of mass transfer.

APPARATUS

A flow diagram of the apparatus used in these experiments is shown in Figure 1. This was essentially the same as the 4-in. column used by Leibson and Beckmann (12) and Wicks and Beckmann (18). All piping, pumps, and metal column parts were type 304 stainless steel. The column was constructed of 4-in. I.D. Pyrex glass pipe sections. When operated as a spray column, two 2-ft. sections were used, giving an effective height of 4.3 ft. from the dispersed-phase distributor to the interface. When operated as a packed column, one 1-ft. and one 2-ft. section were used with 3 ft. of packing. The bottom of the column was fitted with a conical entrance.

The packing used was 1/2 in. unglazed nonporous Raschig rings. A special packing technique was employed in the vicinity of the dispersed-phase distributor to prevent any packing piece from blocking a nozzle. Three 3/8-in. rings were stacked around each nozzle and a 1/2-in. ring placed on top formed a shield around the nozzle tip and prevented any pieces from resting on it. The column was then filled with water and the remainder of the packing dumped over this array of shielded nozzles. The packing was settled by passing an air blast through the column at a velocity sufficient to raise the packing bed and settle it into the densest configuration. Essentially the same packed system properties were obtained each of the two times the column was packed; number of pieces/cu. ft. = 9350, void fraction = 0.602, superficial surface area = 110 sq. ft./cu. ft.

LIQUID-LIQUID SYSTEMS

The organic solvents used in this investigation were obtained from the Shell Chemical Corporation under the following specifications: for M.I.B.C., 97.5 wt. % min. purity, specific gravity (20°/20°C.) 0.807 to 0.809, distillation range 130 to 133°C.; for M.E.K., 99.0 wt. % min. purity, specific gravity (20°/20°C.) 0.805 to 0.807, distillation range 79.0 to 81.0 °C. City tap water was used in all but the first eleven runs, which were made with distilled water. Tests showed there was no measurable difference in the mutual solubilities of distilled water and tap water with the organic solvents, and the results obtained in the extraction column showed no appreciable difference.

Both the water and the solvent layers of the M.I.B.C.-water system were analyzed by refractive index as measured with a Bausch and Lomb precision refractometer. The calibration curve was determined by measuring the refractive

indices of samples of known concentration made from distilled water and purified M.I.B.C. The accuracy of determining the wt. % of M.I.B.C. in water was estimated to be ± 0.03 wt. % and that for water in M.I.B.C. ± 0.07 wt. %.

For the M.E.K.-water system only the water layer could be analyzed by refractive index, with an estimated accuracy of ± 0.05 wt. % M.E.K. in water. The solvent layer could not be analyzed in the same way because the curve of refractive index vs. composition has a plateau in the vicinity of the two-phase region. The composition of this phase was determined by density measurements taken with a Christian Becker specific gravity balance. Calibration was made by measurements on samples of known composition and was supplemented by data from the literature. Estimated accuracy of this determination was ± 0.06 wt. %.

Mutual solubilities for M.I.B.C. and water were measured by the following method: test tubes containing a layer of both purified M.I.B.C. and distilled water were thermostated at least 2 hr. with frequent shaking. Samples were then withdrawn and analyzed by refractive index. This technique could not be used at temperatures above that of the refractometer thermostat as the sample would separate into two layers when put into

the instrument. Values for this region were estimated by extrapolation of the low-temperature results. For the M.E.K.-water system, the solubility data of Ginnings, Plonck and Carter (6) were used. The equilibrium data used for both systems are given in Table 1.

Interfacial tensions were measured with a Du Nouy ring tensiometer. Viscosities were measured for the pure liquids and the saturated liquid layers with calibrated Fenske-Cannon-Ostwald viscosimeters, and densities were measured with pycnometers. The values obtained for these physical properties are listed in Table 6.

EXPERIMENTAL PROCEDURE

During the first runs the operating procedure was as follows: the column was first filled with water, then steady water flow, as indicated by constant interface position, was established at the desired water rate, and then solvent flow was started at the desired rate. During run no. 17, inspection of the translucent polyethylene tubing section below the dispersed-phase distributor revealed that the solvent line leading to the distributor was filled with water. The solvent flowing in this line was in a dispersed condition in the form of droplets and streams battering their way through the stagnant

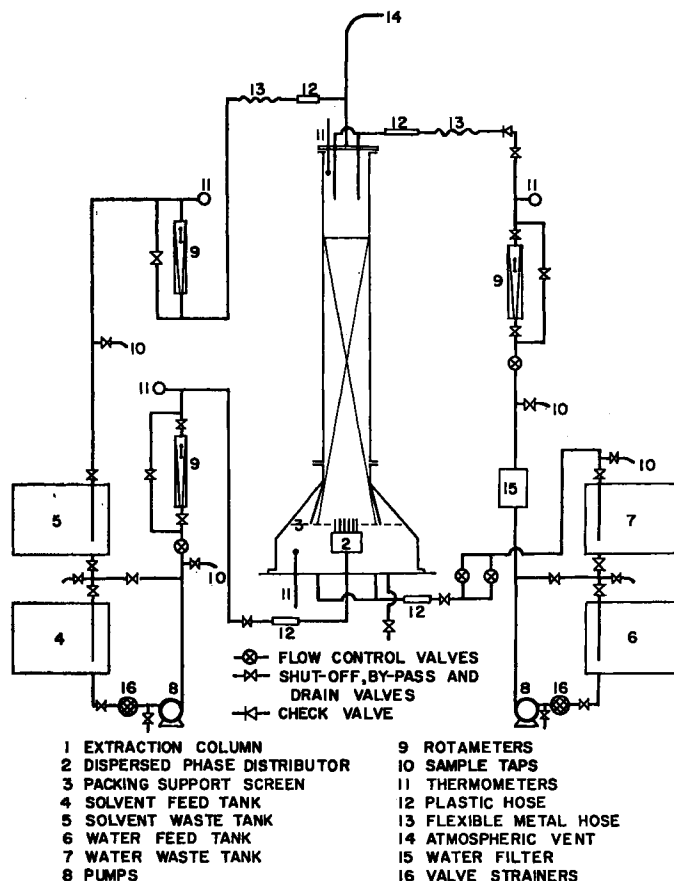


Fig. 1. Flow diagram of extraction equipment.

water. The water apparently had entered the distributor nozzles when the column was first filled with water, displacing any solvent which might be in the distributor and feed line. Accordingly, the solvent leaving the column was more nearly saturated than it should have been, giving unreasonably high coefficients for mass transferring into the dispersed phase. The coefficients also scattered badly, apparently due to differing amounts of water having entered the distributor before each series of runs. This condition was termed back-flooding of water into the distributor.

To remedy this situation the following start-up procedure was instituted:

- Water remaining in the column from the previous series of runs was drained until the interface was below the level of the distributor nozzles.
- The solvent inlet line and distributor were drained to remove any water which had entered during the preceding runs.
- Solvent flow was started at a fairly high rate [about 19 cu. ft./hr. (sq. ft.)].
- When solvent was flowing from all the distributor nozzles, the column was filled with water from the bottom, thus the interface was raised above the distributor with as little disturbance as possible.
- When the interface reached the normal operating level, the water flowing into the bottom of the column was shut off and normal water feed started at the top.
- After stable water flow and interface position had been attained, the solvent flow could be reduced to low values [about 2 cu. ft./hr. (sq. ft.)] without back-flooding. Sudden changes in solvent flow, when operating at these low rates, would often precipitate back-flooding.

The first 35 runs, on the system M.I.B.C.-water in a spray column, were made with a dispersed phase distributor having 48 nozzles, 0.106 in. I.D. When this column was packed, it became difficult to obtain stable operation at low dispersed-phase flow rates. Back-flooding occurred frequently. This may have been caused by obstruction of nozzles by packing pieces and the resultant difficulty of maintaining sufficient solvent flow to prevent water from entering. It was thought that a higher nozzle velocity might help this condition, and accordingly, a distributor having 25 nozzles, 0.106 in. I.D. was installed. To prevent packing pieces from blocking nozzles, the previously described packing method was used. With these modifications stable operation of the packed column on M.I.B.C.-water was attained.

The 25-nozzle distributor was used for all runs on M.E.K.-water. For this system the tendency to back-flood was quite pronounced, and it was impossible to obtain stable operation at dispersed-phase flow rates below 11 cu. ft./hr. (sq. ft.). This effect may have been due to the low-interfacial tension of this

system and the low viscosity of the dispersed phase.

It was found that the column came to equilibrium after two complete changes of the slowest moving phase. The column exit streams were sampled twice during each run: once at the end of two complete changes of the slowest moving phase and again after one more change. The average of the two analyses of each stream was taken for computation of the mass transfer. Feed compositions were analyzed at the beginning and end of each series of runs and the average taken for computation.

When runs were made with the continuous phase presaturated, an amount of organic phase slightly more than sufficient for saturation was added to the water feed drum and mixed by recirculating the water through the pumps and by-pass line. The dispersed phase was presaturated by passing it through the column, which was filled with water, until the total amount of solvent was recirculated three times.

The organic solvents were dehydrated for reuse by salting out. When saturated with water the solvents were passed through a column packed with rock salt. The effluent separated into two layers, the upper being the organic solvent greatly reduced in water content and containing no salt, and the lower the water removed from the solvent and saturated with salt. The solvent layer was withdrawn for reuse and the brine layer discarded. By this method the water content of M.I.B.C. could be reduced to 2.9 wt. % and that of M.E.K. to 3.9 wt. %. No attempt was made to recover solvent from the continuous-phase effluent. As the water became saturated, it was discarded and fresh water drawn.

BASIS OF CALCULATIONS

The number of transfer units for each phase was calculated by the equation,

$$N_t = \ln \frac{y^* - y_1}{y^* - y_2} = \ln \frac{\Delta y_1}{\Delta y_2} \quad (5)$$

The saturation concentration, y^* , was evaluated at the temperature of the stream entering the column for y_1 , and at that of the stream leaving for y_2 . No attempt was made to control temperatures, which varied from 20 to 37°C. as extremes, and were generally in the range 22 to 30°C. Usually all the stream temperatures were within 5°C. of each other in any given run.

Values of the height of a transfer unit were obtained by dividing the effective column height by the number of transfer units. Capacity coefficients of mass transfer were calculated by the equation,

$$k_a = \frac{V}{H_t} \quad (6)$$

where k , V , and H_t are all evaluated for the phase in question. A sample of the data and calculated results for the M.I.B.C.-water system in the packed column are given in Table 2. No attempt was made to check material balances. The amount of material transferred from a phase was so small compared to the amount of the parent phase that the results were meaningless.

RESULTS OF THE EXPERIMENTAL WORK

Flow-rate Effects

The effects of variation in flow rates on the individual mass transfer coefficients are qualitatively the same as those reported by Colburn and Welsh (2) and Laddha and Smith (11). For the dispersed phase H_t is a constant, and for the continuous phase it is a power function of the flow rate ratio. Equations (2) and (3) may be used to correlate the results. The constant C_1 was determined by taking the mean of the $(H_t)_d$ values. The values of $(H_t)_c$ were plotted vs. V_d/V_c on log-log coordinates and fitted with straight lines by the method of least squares (Figures 2-5). Values of these constants, along with those obtained in other investigations, are listed in Table 3.

As a test of the reliability of these correlations, several statistical measures were computed. This was also done for the results of Colburn and Welsh (2) and of Gayler and Pratt (4). These statistics are included in Table 3. The 95% confidence limits were computed for C_1 , the mean of $(H_t)_d$. As these limits are fairly narrow, there appear to be significant differences among the values of C_1 for the different systems. The 95% confidence limits for the mean of $(H_t)_c$ are a measure of the reliability of C_2 . Again, the values for the different systems are significantly different. For the slope, n , the confidence limits at the 95% level are fairly wide and there is some overlapping. This indicates some uncertainty as to whether all the values of n reported in Table 3 are really different from each other. However, the fact that some of these confidence bands do not overlap indicates that some real differences do exist. For the $(H_t)_c$ vs. V_c/V_d correlation, the correlation coefficient, r , was also computed. The square of this quantity is the fraction of the variation in $(H_t)_c$ which is dependent on variations in V_c/V_d , the rest being variation due to other causes including sampling and analytical errors. For the present work r^2 is 0.89 to 0.95, for the data of Gayler and Pratt (4) it is 0.85, and for that of Colburn and Welsh (2) 0.75. These statistics were not computed for the results of Laddha and Smith (11) because their complete data were not available.

Most of the runs in the packed column were made in the region below loading. Several runs were made which appeared

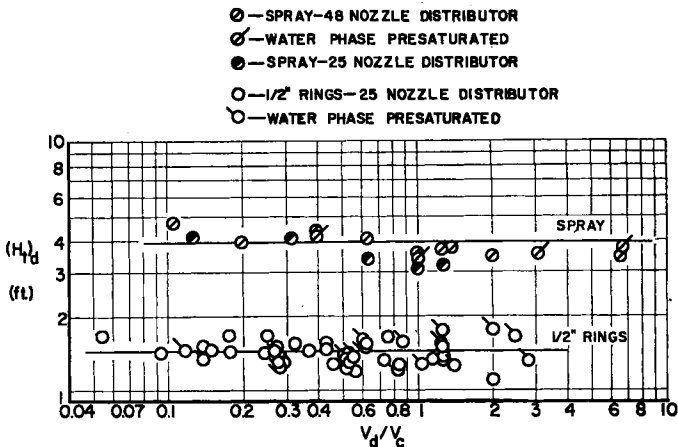
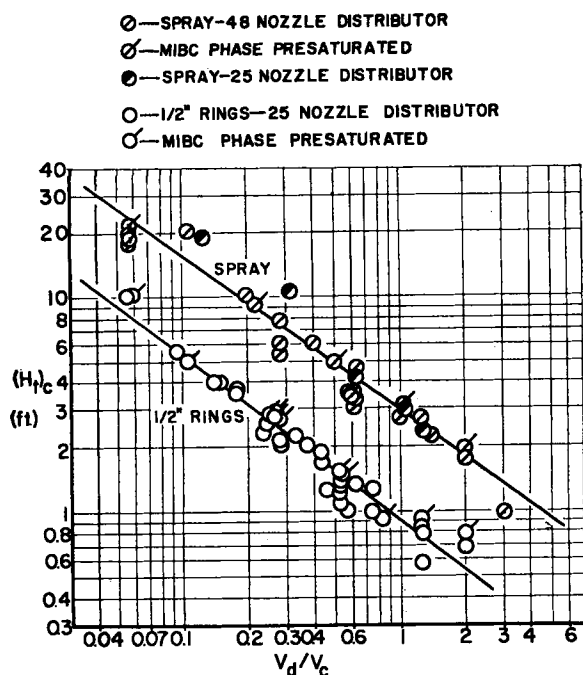


Fig. 3. M.I.B.C.—water system.

Fig. 2. M.I.B.C.—water system.

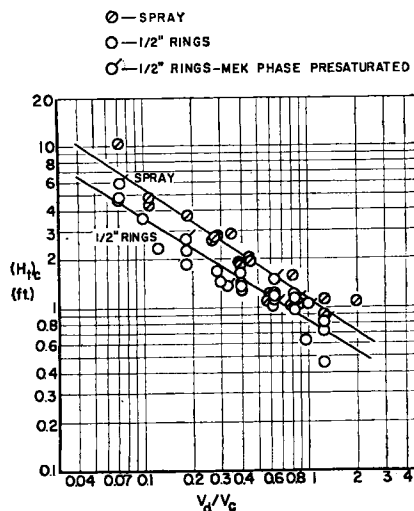


Fig. 4. M.E.K.—water system.

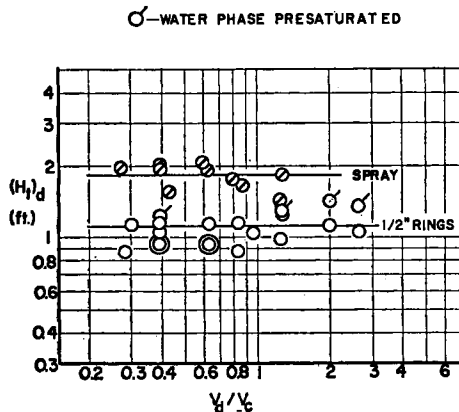


Fig. 5. M.E.K.—water system.

to be in the loading region and are noted in the complete tabulation of experimental data. Spray column operation was always in the region below loading.

The results plotted in the form of ka vs. V_d (Figures 6 and 7) provide more insight into the operation of the column than the correlation presented above. The capacity coefficient for the dispersed phase is a linear function of the dispersed-phase flow rate, with little continuous phase effect. If it is assumed that k_d is a constant for a given system, it would appear that a is a linear function of V_d . Under these conditions $(H_t)_d$ will be a constant. Since k_d for a given system is probably dependent on the shear conditions at the droplet surface, it seems reasonable to assume that k_d is constant for a given system in a given

packing because the average velocity of the droplets will be constant provided the dispersed-phase feed rate is not so high as to cause bunching and coalescence of the droplets (i.e., loading). The total surface area of the droplets will be a direct function of dispersed-phase flow rate if the average droplet size is independent of the flow rate. Hayworth and Treybal (8) found that there is little variation in the diameter of droplets issuing from nozzles at nozzle velocity less than 10 cm./sec. Lewis, Jones, and Pratt (14) found the droplet diameter to be independent of dispersed-phase flow rate and packing size in packings $\frac{1}{2}$ in. or larger at flow rates below loading. The equation they propose for surface area is a direct function of V_d .

The capacity coefficient for the continuous phase is a function of both flow rates. If k_c were constant and a is a linear function of V_d , one would expect $k_c a$ to be a linear function of V_d only, and $(H_t)_c$ to be a linear function of

V_c/V_d . However, $k_c a$ is not only a function of V_d but is also, to a lesser extent, a function of V_c . This causes $(H_t)_c$ to be a function of $(V_c/V_d)n$, where n varies from 0.6 to 0.9 for various systems.

The condition of water back-flooding into the dispersed-phase distributor, mentioned above, caused low values of $(H_t)_d$ with considerable scattering in the early runs. The improved start-up procedure, which prevented water's entering the distributor, corrected these conditions. Since the bulk of the water phase was contacting solvent droplets in the normal manner, there was no effect on $(H_t)_c$.

The first 35 runs on M.I.B.C.-water in a spray column were made with a distributor having 48 nozzles, 0.106 in. diam. With this distributor the nozzle velocity did not exceed 10 cm./sec., the velocity where Hayworth and Treybal (8) claim nonuniform droplet formation begins. However, at very low dispersed-phase flow rates the nozzle velocity was so low that back-flooding of water into the distributor frequently occurred, and this difficulty became more pronounced when the column was packed. To remedy this, a distributor originally designed for a 3-in. column, having 25 nozzles of the same diameter, was used. With this modification, stable operation without back-flooding was attained even at low dispersed-phase flow rates. However, above $V_d = 24$ cu. ft./hr.(sq. ft.), the nozzle velocity exceeded 10 cm./sec., and going as high as 15 cm./sec. Visually, it did appear that there were more small droplets in the column. Therefore, a series of 5 more runs were made with M.I.B.C.-water in a spray column with the 25-nozzle distributor. The results were not

TABLE 2.
SAMPLE MASS TRANSFER DATA—M.I.B.C.-WATER—4-IN. COLUMN, 1/2-IN. RASCHIG RINGS

Run No.	Flow rates (ft./hr.)		Temperatures (°C.)				Concentrations and concentration gradients (wt. %)			
	V_c	V_d	T_c		T_d		water phase			
			Inlet	Outlet	Inlet	Outlet	X_1	ΔX_1	X_2	ΔX_2
66	28.6	3.91	27.1	27.0	25.6	26.9	0	1.66	0.87	0.79
67	28.6	7.75	27.2	27.2	28.3	27.0	0	1.65	1.20	0.45
68	28.6	15.0	19.0	25.4	31.3	19.6	0	1.90	1.55	0.16
70	28.6	29.0	19.2	28.5	35.7	19.8	0	1.89	—	—
73	12.0	3.0	19.5	20.5	24.5	19.6	0	1.88	1.18	0.68
74	12.0	7.5	21.8	23.2	28.5	21.8	0	1.82	1.57	0.20
75	12.0	15.0	24.6	28.3	33.4	24.3	0	1.73	1.59	0.04
76	12.0	24.0	27.5	35.1	37.8	28.1	0	1.65	1.45	0.02
77	53.0	7.9	21.7	22.3	25.4	21.8	0	1.82	0.91	0.89
78*	53.0	15.0	21.7	22.9	27.3	21.9	0	1.82	1.34	0.44
79*	53.0	24.0	21.8	24.3	29.3	22.0	0	1.82	1.59	0.15
80*	53.0	29.7	22.0	25.4	33.0	22.2	0	1.82	1.62	0.09

Run No.	M.I.B.C. phase				(ft.)				(1/hr.)	
	Y_1	ΔY_1	Y_2	ΔY_2	$(N_1)_c$	$(N_1)_d$	$(H_1)_c$	$(H_1)_d$	$k_a a$	$k_d a$
66	3.19	3.19	6.00	0.44	0.742	1.981	4.04	1.51	7.09	2.59
67	3.19	3.32	6.00	0.44	1.299	2.02	2.31	1.49	12.39	5.20
68	3.19	3.47	5.85	0.29	2.475	2.48	1.21	1.21	23.6	12.40
70	3.19	3.75	5.78	0.36	—	2.34	—	1.28	—	22.7
73	2.95	3.39	5.57	0.56	1.031	1.800	2.91	1.67	4.12	1.80
74	2.95	3.56	5.71	0.51	2.21	1.942	1.36	1.54	8.82	4.87
75	2.95	3.85	5.92	0.40	3.77	2.26	0.795	1.33	15.10	11.28
76	2.95	4.13	6.23	0.27	4.41	2.72	0.680	1.10	17.65	21.8
77	3.01	3.36	5.78	0.44	0.715	2.04	4.20	1.47	12.62	5.38
78*	3.01	3.45	5.85	0.37	1.420	2.23	2.11	1.34	25.1	11.20
79*	3.01	3.54	5.89	0.34	2.41	2.34	1.25	1.28	42.5	18.76
80*	3.01	3.76	5.93	0.31	3.00	2.50	1.00	1.20	53.0	24.8

*Flooding

significantly different from those of the earlier runs. Apparently, the nonuniformity of droplet formation does not become great in this range, or it may be compensated by changes in the holdup. All subsequent runs were made with the 25-nozzle distributor. With the M.E.K.-water system the tendency to back-flood was increased by the lower interfacial tension and it became impossible to obtain reliable values for the dispersed-phase film below $V_d = 11$ cu. ft./hr. (sq. ft.).

Another difficulty encountered with the M.E.K.-water system was a change in the volumetric-phase flow rate through the column, a result of the fact that M.E.K. is more soluble in water than water is in M.E.K. Under the worst conditions, at high V_c and low V_d , there was a 25% increase in V_c and a 50% decrease in V_d . To prevent this, the water phase was preloaded with M.E.K. so that the amount of M.E.K. it would take up in the column would correspond to the amount of water going into the M.E.K. phase. This did not completely eliminate the difficulty, but it did keep the volumetric-phase changes to less than 10%. A correction was applied to the H_i values based on the assumption that if the volumetric flow rate of the dispersed phase decreased by the factor f , the total surface area of the dispersed-phase droplets will decrease by $f^{2/3}$. For the M.I.B.C.-water system under the worst conditions, V_c increased by less than 1%

and V_d decreased by 9%. For most runs the volumetric-phase change was much less so that no correction was applied to the M.I.B.C.-water results. These changes in volumetric flow rates may account for the greater scattering of the M.E.K.-water data.

Because of the salting-out technique used to dehydrate the solvents for reuse, the initial water concentration of the solvent was about 3 wt. % for M.I.B.C., and 4 wt. % for M.E.K. in most runs. Pure water was used as continuous-phase feed when M.I.B.C. was the dispersed phase. With M.E.K. dispersed, the initial solvent concentration of the water phase was 12 to 20 wt. % M.E.K.

Area-based Coefficients

The H_i values obtained for packed column, may be reduced to area-based coefficients by the use of Gayler and Pratt's (3) expression for surface area,

$$a = \frac{6\epsilon x'}{d_{v,}} = \frac{6V_D}{d_{v,}^0 \bar{v}_0} \quad (7)$$

The quantities $d_{v,}^0$ and \bar{v}_0 represent, respectively, the characteristic droplet size and characteristic droplet velocity. They are constants for a given system and a given packing size and are the quantities used to correlate droplet size, holdup, and surface area with system physical properties and packing characteristics.

As Pratt and his associates (14, 3) have

noted, this expression can only be regarded as a first approximation to the surface area. In their droplet studies they could only photograph droplets entering and leaving packed sections and were unable to measure droplet size and shape within the packing. In their holdup studies they were unaware of the complex phenomena revealed by the studies of Wicks (18) and Marks (15) on the rate of displacement of permanent holdup and hysteresis holdup. The work of these latter investigators was confined to a single system and has not yet been generalized for application to other liquid-liquid systems. However, it seems reasonable to assume that the free holdup, which is a linear function of V_d below the loading point and which is usually about 90% of the total holdup, represents better than 90% of the effective area for mass transfer. The slower moving permanent holdup tends to coalesce and become saturated and is therefore less effective in mass transfer.

Applying Gayler and Pratt's (3) surface area equation to Equations (2), (3), and (6) yields,

$$k_d = \frac{d_{v,}^0 \bar{v}_0}{6(H_1)_d} \quad (8)$$

$$k_c = \frac{d_{v,}^0 \bar{v}_0}{6(H_1)_c} \cdot \frac{V_c}{V_D} = \frac{d_{v,}^0 \bar{v}_0}{6C_2} \left(\frac{V_c}{V_D} \right)^{1-n} \quad (9)$$

and the numerical results in Table 4. In the case of the M.E.K.-water system, these results may be compared to those of Murphy, Lastovica, and Skrzec (16) obtained in a horizontal extraction tube where the surface area could be measured accurately. For k_d , the rate of transfer of water into ketone, the results of the present study are equal to those obtained by Murphy, et al. (0.091 to 0.104 ft./hr.), at high rates of interfacial shear, comparable to that found at the surface of a rising droplet. For k_c , Murphy's highest results are about one-half those of this study (0.030 to 0.076 ft./hr.).

Effect of Presaturation

Presaturation of either phase makes no perceptible difference in the results. This method of operation could affect the results in two ways: presaturation of water with solvent could present a resistance to diffusion of water from the bulk phase to the interface, and similarly for solvent presaturated with water, or presaturation might change the droplet diameter, thereby causing a change in the surface area available to mass transfer. Apparently, neither of these effects was present in this investigation.

Gayler and Pratt (4) claim that $(H_1)_d$ is about 10% lower when the aqueous phase is presaturated and explain this on the basis of a decreased droplet diameter. They made no measurements for the case of presaturated organic phase.

Comparison of Spray Column and Packed-column Operation

In a system of moderately high interfacial tension (6 dynes/cm.), H_i values for spray columns are about three times those for $\frac{1}{2}$ -in. ring packing. For a low interfacial-tension system (1 dyne/cm.) the improvement is only about 30%. This may be explainable on the basis of droplet diameters. For the higher interfacial-tension system the droplet diameter appears to be much greater in a spray column than in a packed column. For the lower interfacial-tension system the droplet diameter appears to be about the same for the two methods of operation. These observations are purely qualitative since no provision was made for measurement of droplet diameters. For packed-column operation a fairly good estimate could be made by visual comparison of the droplet diameters with packing pieces whose dimensions are known.

The available correlations for droplet diameters do not furnish support for the above view (Table 5). Observations would indicate that the droplets predicted for M.E.K.-water by Hayworth and Treybal (8) are too large. It is worth noting that in deriving this correlation no data were taken on systems having an interfacial tension lower than about 6 dynes/cm. Also, in the Hayworth and Treybal correlation, for nozzle velocities about 10 cm./sec., where nonuniform droplet formation begins, only the largest droplet diameter is given. Under these conditions the average volume-surface diameter (d_{vs}) would be smaller than the predicted diameter.

COMPARISON WITH PREVIOUS WORK

Three previous studies employing binary liquid-liquid system in packed or spray columns are available for comparison with the present results. The pioneer study was done by Colburn and Welsh (2) using the system isobutanol-water. Two series of experiments were made; one with isobutanol dispersed and one with water dispersed. The column was of 3.75 in. diam., packed with 1.75 ft. of $\frac{1}{2}$ in. clay Raschig rings. Their results are presented in Table 4, the points having been recalculated to a basis of 3 ft. of packing with the end effects determined by Gayler and Pratt (4). This latter work was done on a different liquid-liquid system in a 4-in. column with $\frac{1}{2}$ in. rings and may not be strictly applicable to the isobutanol-water system. However, it is the only work available on end effects in extraction column operation on binary systems, and it is felt that these corrected points offer a better basis for comparison with the present work. The corrected points were fitted by the method of least squares.

Laddha and Smith (11) studied the systems 3-pentanol-water and isobutyraldehyde-water in a 2-in. column packed with $\frac{1}{4}$ -in. and $\frac{3}{8}$ -in. Raschig rings, and also operated as a spray column. Packed heights were 2.2 ft. for 3-pentanol-water and 4.2 ft. for isobutyraldehyde-water. Two sets of experiments were made on each

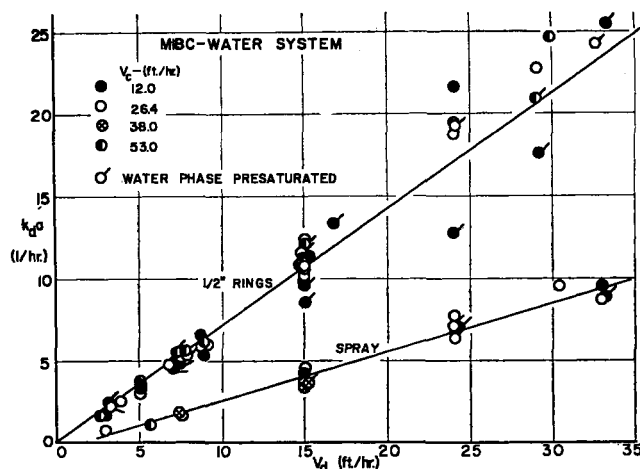


Fig. 6. M.I.B.C.-water system.

TABLE 3
CONSTANTS FOR MASS TRANSFER CORRELATIONS

Dispersed phase	Continuous phase	Packing	C_1 (ft.)*	C_2 (ft.)*	n^*
M.I.B.C.	water	spray	3.99 ± 0.52	2.91 ± 0.47	0.723 ± 0.082
M.E.K.	water	spray	1.83 ± 0.15	1.12 ± 0.22	0.687 ± 0.123
Isobutyraldehyde	water	spray	—	2.80	0.54
water	Isobutyraldehyde	spray	2.5	—	—
3-Pentanol	water	spray	1.15	0.81	0.96
water	3-Pentanol	spray	0.80	1.75	0.83
M.I.B.C.	water	$\frac{1}{2}$ -in. rings	1.44 ± 0.05	0.903 ± 0.10	0.775 ± 0.060
M.E.K.	water	$\frac{1}{2}$ -in. rings	1.11 ± 0.08	0.824 ± 0.12	0.630 ± 0.085
EtAc	water	$\frac{1}{2}$ -in. rings	0.81 ± 0.05	1.70 ± 0.09	0.543 ± 0.061
Isobutanol	water	$\frac{1}{2}$ -in. rings	1.04 ± 0.06	1.30 ± 0.27	0.795 ± 0.173
water	Isobutanol	$\frac{1}{2}$ -in. rings	0.64 ± 0.04	2.16 ± 0.20	0.610 ± 0.120
Isobutyraldehyde	water	$\frac{3}{8}$ -in. rings	—	2.58	0.58
water	Isobutyraldehyde	$\frac{3}{8}$ -in. rings	2.5	—	—
3-Pentanol	water	$\frac{3}{8}$ -in. rings	0.75	0.63	0.94
water	3-Pentanol	$\frac{3}{8}$ -in. rings	0.80	1.58	0.87
Isobutyraldehyde	water	$\frac{1}{4}$ -in. rings	—	2.21	0.58
water	Isobutyraldehyde	$\frac{1}{4}$ -in. rings	2.5	—	—
3-Pentanol	water	$\frac{1}{4}$ -in. rings	0.75	0.61	0.98
water	3-Pentanol	$\frac{1}{4}$ -in. rings	0.80	1.38	0.87

*95 % confidence limits shown by \pm

system: one with the organic phase dispersed and one with the water phase dispersed. No attempt was made to correct the results to equivalence with 3 ft. of packing because the available data on end effects were not only for a different system, but also for a different packing size. The correlations as presented by Laddha and Smith were fitted by least squares. As the flow rates were originally given in terms of weight units, lb./hr.(sq. ft.), these correlations have been corrected for use with flow rates in volumetric terms, cu. ft./hr.(sq. ft.). The corrected correlations are given in Table 3. Because no reliable analytical method was available for water in isobutyraldehyde, no data on the isobutyraldehyde film are given. The Laddha and Smith (11) results show little difference between spray columns and packed columns with either $\frac{1}{4}$ in. or $\frac{3}{8}$ in. packing, which may have been due to the small distributor nozzles used, 0.043 in. diam. This would have given small droplets

for spray-column operation. The Hayworth and Treybal (8) correlation predicts droplets 1.0 to 2.1 mm. diam. for the spray column with 3-pentanol-water, either phase dispersed. In a packed system the Lewis, Jones, and Pratt (14) correlation predicts 2.3 mm. for 3-pentanol dispersed and 4.4 mm. for water dispersed in packings above the critical size. For these low interfacial-tension systems, the critical packing size may be as small as $\frac{1}{4}$ in.

Gayler and Pratt (4) employed the system ethyl acetate-water in a 4-in. column packed with $\frac{1}{2}$ in. clay Raschig rings. Packed heights of $\frac{1}{2}$, 1, 2, and 3 ft. were used in order to determine end effects. Runs with the aqueous phase presaturated were also made. Holdup data were taken to determine the characteristic droplet velocity, \bar{v}_0 , for use in Equation (7) in order to express the results in terms of area-based coefficients. For comparison with the present work their results have been correlated by the Colburn and Welsh-type

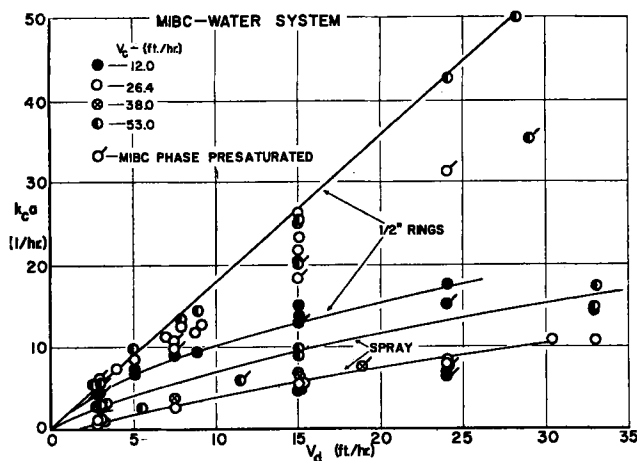


Fig. 7. M.I.B.C.-water system.

TABLE 4
AREA-BASED COEFFICIENTS

System	Water into solvent k_d (ft./hr.)	Solvent into water k_c (ft./hr.)	Range of k_c covered in experiments
M.I.B.C.-water	0.356	$0.567 (V_c/V_d)^{0.225}$	0.486 — 1.090
M.E.K.-water	0.106	$0.144 (V_c/V_d)^{0.370}$	0.133 — 0.382
EtAc-water	0.927	$0.444 (V_c/V_d)^{0.457}$	0.155 — 1.11

TABLE 5
DROPLET DIAMETERS

System	d_{spray} (mm.) (Hayworth and Treybal (8))	$d_{e,\text{packed}}$ (mm.) (Lewis, Jones and Pratt (14))	$d_{u,\text{g-packed}}$ (mm.) (observed)
M.I.B.C.-water	4.2	2.18	2.4
M.E.K.-water	2.5 — 4.0	1.45	1.0

equations (Figures 8-9). The points for 3 ft. and 2 ft. of packing are shown here, those for 2 ft. having been corrected to equivalence with 3 ft. of packing. Some low values of $(H_t)_d$ were obtained at low values of V_d , which may have been caused by water back-flooding into the distributor. At higher dispersed-phase flow rates this water could have been displaced from a distributor of the type employed in their column, in which case the values obtained at these higher flow rates would be the true $(H_t)_d$ values. As there were also some unusually high values at the higher V_d/V_c ratios, the mean of all the $(H_t)_d$ points was taken for C_1 , which lies close to the majority of the points.

Physical Property Effects

The effect of physical properties of the liquid-liquid systems on mass transfer rates was investigated by attempting to correlate the constants of the Colburn and Welsh-type equations, listed in Table 3, with the physical properties in the form of dimensionless groups. In these attempts the physical properties considered were μ_c , μ_d , ρ_c , ρ_d , γ and the diffusivities. The values of these properties used in the correlations are listed in Table 6. The viscosities and densities

are those reported by the experimenters. Interfacial tensions were measured by Gayler and Pratt (4) for ethyl acetate-water, and by the author for M.I.B.C.-water and M.E.K.-water. For isobutanol-water and 3-pentanol-water, values were taken from the literature (10). No interfacial tension data could be found for the isobutyraldehyde-water system. Diffusivities were estimated by the method of Chang and Wilke (1) except for the system isobutanol-water where experimental values were available from the work of Heertjes, Holve and Talsma (9). All values reported in Table 6 are at the mean temperatures and concentrations of the experiments to which they apply. While the extremes of temperature variation were from 20 to 37°C., the majority of runs were in the range of 22 to 30°C. Temperature effects in the dimensionless groups used in the correlation would tend to be self-compensating and temperature variations in the above range will not have any great effect on the correlations.

The exponent n appears to be a function of the viscosity ratio. This is shown on a semilogarithmic plot in Figure 10. The six points lying above the others are all the points for the 3-pentanol-water

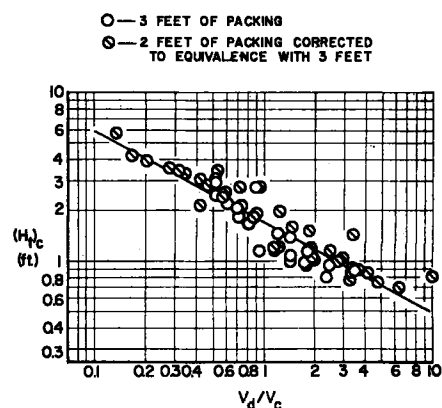


Fig. 8. Data of Gayler and Pratt. Ethyl acetate-water system.

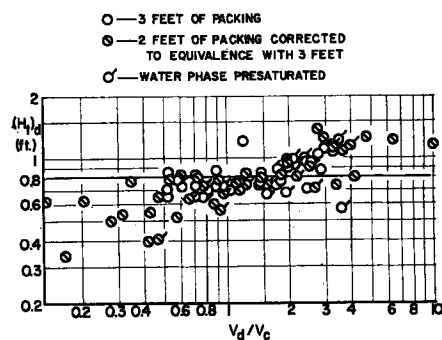


Fig. 9. Data of Gayler and Pratt. Ethyl acetate-water system.

system. It is difficult to say whether this deviation is caused by deficiencies in the experiments or represents a real effect. The remaining points suggest that n may be related to μ_c/μ_d by a function of the following form:

$$n = a + b \ln \left(\frac{\mu_c}{\mu_d} \right) \quad (10)$$

This says that the manner in which the flow-rate ratio affects $(H_t)_d$ is a function of (μ_c/μ_d) . This may be explainable as the effect of viscosity ratio upon the interfacial shear conditions at the droplet surface, or upon the relative amounts of turbulence or circulation within the droplets or in the continuous phase adjacent to the droplet surface.

Several different dimensionless groupings of the physical properties were tried in attempts to correlate the coefficient C_2 . The best result is shown in Figure 11. The four low points, for $1/4$ -in. and $3/8$ -in. rings are all for the 3-pentanol-water system which also caused deviations in Figure 9. In this case the deviation may be due to the fact no correction for end effects was made on these points. The reason for the one high point, M.I.B.C.-water in spray-column operation, is unknown. From these points it appears that C_2 may be a function of the $1/4$ power of the groups $(d\Delta\rho\gamma/\mu_c^2)$, (μ_c/μ_d) and $(N_{Sc})_c$. In the

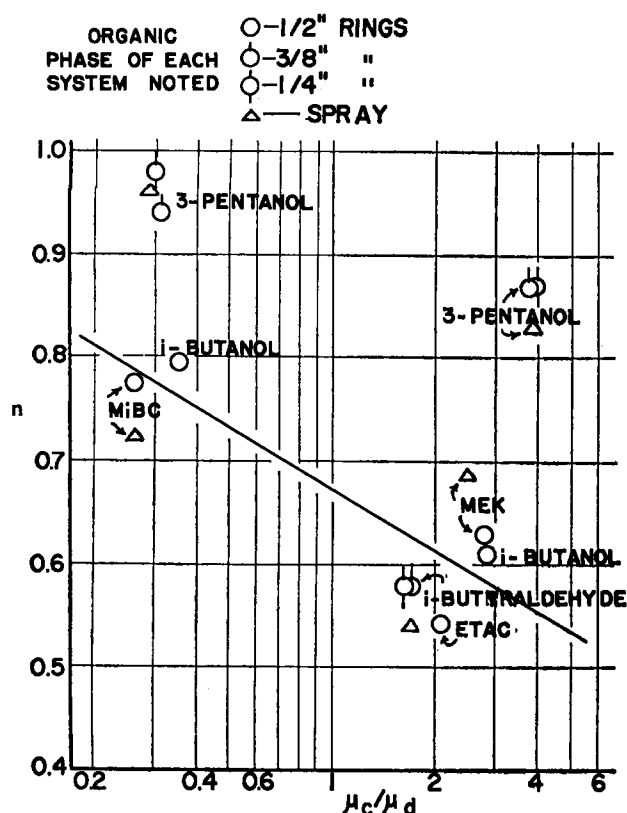


Fig. 10. Effect of physical properties on mass transfer.

first group d is the droplet diameter as predicted by Hayworth and Treybal's correlation (8) for spray columns, or Lewis, Jones, and Pratt's (14) for packed columns. This group may account for the effect of changing droplet diameter, density difference, and interfacial tension upon the surface area available to mass

transfer. The viscosity ratio may account for surface shear conditions or circulation conditions as mentioned above. The Schmidt number may be regarded as accounting for the mass transfer by molecular diffusion in the surface film. There is considerable evidence that eddy diffusion plays a more significant part in

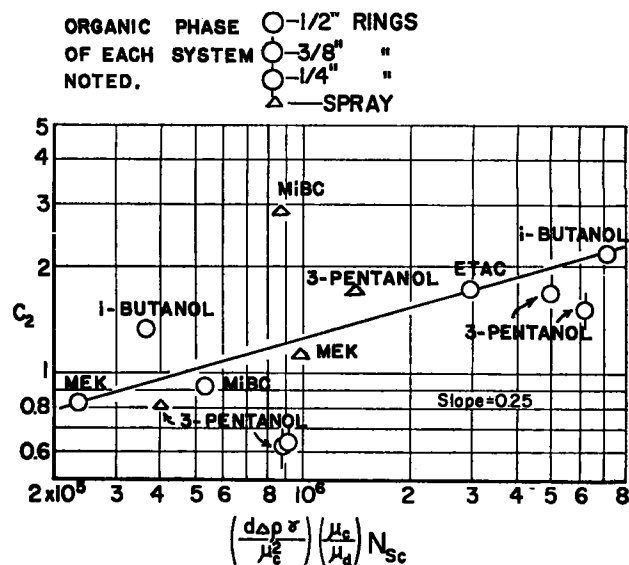


Fig. 11. Effect of physical properties on mass transfer.

mass transfer in liquids than does molecular diffusion. However, the lack of eddy diffusivities and viscosities makes it impossible to include such effects in a correlation of this kind. In any case, the correlations attempted which did not include the Schmidt number were not as good as those presented in Figure 11.

Combining these two correlations leads to an equation of the form,

$$(H_t)_c = (\text{const}) \left(\frac{d\Delta\rho\gamma}{\mu_c^2} \right)^{1/4} \cdot \left(\frac{\mu_c}{\mu_d} \right)^{1/4} (N_{Sc})_c^{1/4} \left(\frac{V_c}{V_d} \right)^n \quad (11)$$

TABLE 6
PHYSICAL PROPERTIES AND DIMENSIONLESS GROUPS

Dispersed phase	Continuous phase	μ_c/μ_d	$\Delta\rho$ (g./cc.)	γ (dynes/cm.)	d (mm.)	$\frac{d\Delta\rho\gamma}{\mu_c^2}$	D_{dc} (sq. cm./sec. $\times 10^6$)	D_{cd}	$\frac{\mu_c}{D_{dc}\rho_c}$	$\frac{\mu_d}{D_{cd}\rho_d}$
Spray columns										
M.I.B.C.	Water	0.262	0.193	6.11	4.4	6550	15	20	603	2100
M.E.K.	Water	2.44	0.167	0.95	3.7	484	15	130	825	44.5
Isobutyraldehyde	Water	1.69	0.200	—	1.1	—	11.5	96	760	78
Water	Isobutyraldehyde	0.706	0.200	—	1.1	—	96	11.5	78	760
3-Pentanol	Water	0.29	0.190	5.0	1.1	1412	8.7	11.5	1000	3320
Water	3-Pentanol	3.79	0.190	5.0	1.1	109	11.5	8.7	3320	1000
Packed columns										
(1/2 in. rings, 4 in. column)										
M.I.B.C.	Water	0.262	0.193	6.11	2.3	3440	15	20	603	2100
M.E.K.	Water	2.78	0.167	0.95	1.0	101	15	130	825	44.5
EtAc	Water	2.08	0.093	6.5	3.5	2120	17	148	669	36
Isobutanol	Water	0.354	0.163	2.1	2.3	586	7.0	2.4	1760	17400
Water	Isobutanol	2.81	0.163	2.1	3.8	146	2.4	7.0	17400	1760
(3/8 in. rings, 2 in. column)										
Isobutyraldehyde	Water	1.69	0.200	—	—	—	11.5	96	760	78
Water	Isobutyraldehyde	0.591	0.200	—	—	—	96	11.5	78	760
3-Pentanol	Water	0.31	0.190	5.0	2.3	3110	8.9	12.0	940	3040
Water	3-Pentanol	3.72	0.190	5.0	4.4	435	12.0	8.9	3040	940
(1/4 in. rings, 2 in. column)										
Isobutyraldehyde	Water	1.65	0.200	—	—	—	10.9	96	850	78
Water	Isobutyraldehyde	0.606	0.200	—	—	—	96	10.9	78	850
3-Pentanol	Water	0.30	0.190	5.0	2.3	3110	8.8	10.8	960	3720
Water	3-Pentanol	3.87	0.190	5.0	4.4	435	10.8	8.8	3720	960

This equation is presented only as a tentative method of correlation. Data on many more systems will be needed before it can be established with any certainty.

The constant C_1 apparently cannot be correlated with physical properties by the data now at hand. This may be due to inaccuracies in the values of $(H_i)_d$, especially in tall columns where the dispersed phase often approaches saturation. The condition of continuous phase back-flooding into the distributor may also have been present in the earlier work.

SUMMARY OF RESULTS

The individual film coefficients of mass transfer have been measured for two binary liquid-liquid systems in a packed extraction column and in a spray column. The two systems were methyl isobutyl carbinol-water and methyl ethyl ketone-water. In each case the organic phase was dispersed. The column was 4 in. I.D. In spray-column operation the effective column height was 4.3 ft. and in packed-column operation it was packed with 3 ft. of 1.2 in. Raschig rings.

The results may be summarized as follows:

1. The individual mass transfer coefficients for each system can be correlated by the Colburn and Welsh type of equations,

$$(H_i)_d = C_1$$

$$(H_i)_c = C_2(V_c/V_d)^n$$

2. The H_i values can be reduced to area-based coefficients by the expression for surface area proposed by Gayler and Pratt (3),

$$a = \left(\frac{6V_d}{d_{0..}^3 \bar{v}_0} \right)$$

This yields

$$k_d = \frac{d_{0..}^2 \bar{v}_0}{6(H_i)_d}$$

and

$$k_c = \frac{d_{0..}^2 \bar{v}_0}{6C_2} \left(\frac{V_c}{V_d} \right)^{1-n}$$

The values of k obtained for the M.E.K.-water system compare favorably with those found by Murphy, Lastovica, and Skrzec (16) for this same system in a horizontal-tube extractor where the surface area available to mass transfer is known.

3. Presaturation of either phase makes no perceptible difference in the results for either system.
4. In systems of low interfacial tension, spray columns are almost as efficient as packed columns due to the small droplets formed. In systems of high interfacial tension packed columns are considerably more efficient than spray columns.

5. The exponent n in the correlating equation for $(H_i)_c$ appears to be a function of the viscosity ratio, possibly of the form,

$$n = a + b \ln (\mu_c/\mu_d)$$

The coefficient C_2 of the same equation appears to be a function on the $1/4$ power of the groups $(d\Delta\rho\gamma/\mu_c^2)$, (μ_c/μ_d) and $(N_{Sc})_c$. Combining these two functions leads to a correlating equation of the following form.

$$(H_i)_c = \text{const} \left(\frac{d\Delta\rho\gamma}{\mu_c^2} \right)^{1/4} \left(\frac{\mu_c}{\mu_d} \right)^{1/4} (N_{Sc})_c^{1/4} \left(\frac{V_c}{V_d} \right)^n$$

This correlation is only a tentative proposal. More data on other liquid-liquid systems are needed to confirm the nature of this relationship.

6. The available data for $(H_i)_d$ do not appear to correlate with the physical properties of the liquid-liquid systems.

ACKNOWLEDGMENT

The financial assistance of E. I. du Pont de Nemours and Company and the Allied Chemical and Dye Corporation, each of which provided fellowship assistance to one of the authors, has been greatly appreciated.

NOTATION

- a = area of contact of the phases per unit volume of the column, sq. ft./cu. ft.
 C_1 = coefficient in empirical mass transfer correlation
 C_2 = coefficient in empirical mass transfer correlation
 d = droplet diameter, ft.
 $d_{0..}$ = mean volume-surface diameter of droplets = $(\Sigma nd^3/\Sigma nd^2)$ - ft.
 $d_{0..}^0$ = characteristic droplet diameter, i.e., the value of $d_{0..}$ at zero flow rates, ft.
 D = molecular diffusivity, sq. ft./hr.
 H_i = height of a transfer unit, individual, ft.
 k = mass transfer coefficient, individual, lb./hr.(sq. ft.)(lb./cu. ft.), i.e., ft./hr.
 n = exponent in empirical mass transfer correlation
 N_i = number of transfer units
 N_{Sc} = Schmidt number $\mu/\rho D$
 T = temperature, °C.
 V = superficial velocity of phase in empty column, cu. ft./hr.(sq. ft.)
 \bar{v} = mean velocity of droplets relative to packing, ft./hr.
 \bar{v}_0 = characteristic velocity of droplets, i.e., mean velocity of droplets at zero flow rates, ft./hr.

- x = weight fraction of organic phase in continuous water phase
 x^i = fractional holdup of dispersed phase in packing voids
 y = weight fraction of water phase in dispersed organic phase

Greek Letters

- γ = interfacial tension, lb./hr.)² or dynes/cm. (= g./sec.)²
 ϵ = fractional voidage of packing
 μ = absolute viscosity, lb./hr.(ft.)
 ρ = density—lb./cu. ft.

Subscripts

- avg = arithmetic average
 c = continuous phase
 d = dispersed phase
 i = value at interface
 lm = logarithmic mean
 $1, 2$ = entrance and exit conditions of phase, respectively

Superscript

- * = value at equilibrium or saturation

LITERATURE CITED

1. Chang, Pin, and C. R. Wilke, *A.I.Ch.E. Journal*, **1**, 264 (1955).
2. Colburn, A. P., and D. G. Welsh, *Trans. Am. Inst. Chem. Engrs.*, **38**, 179 (1942).
3. Gayler, R., and H. R. C. Pratt, *Trans. Inst. Chem. Engrs. (London)*, **31**, 69 (1953).
4. Gayler, R., and H. R. C. Pratt, *Trans. Inst. Chem. Engrs. (London)*, **31**, 78 (1953).
5. Gayler, R., N. W. Roberts, and H. R. C. Pratt, *Trans. Inst. Chem. Engrs. (London)*, **31**, 57 (1953).
6. Ginnings, P. M., D. Plonck, and E. Carter, *J. Am. Chem. Soc.*, **62**, 1923 (1940).
7. Gordon, K. F., and T. K. Sherwood, *Chem. Eng. Progr., Symposium Ser.*, No. 10, 15 (1954).
8. Hayworth, C. B., and R. E. Treybal, *Ind. Eng. Chem.*, **42**, 1174 (1950).
9. Heertjes, P. M., W. A. Holve, and H. Talsma, *Chem. Eng. Sci.*, **3**, 122 (1954).
10. "International Critical Tables," **4**, 432, McGraw-Hill, New York (1928).
11. Laddha, G. S., and J. M. Smith, *Chem. Eng. Progr.*, **46**, 195 (1950).
12. Leibson, I., and R. B. Beckmann, *Chem. Eng. Progr.*, **49**, 405 (1953).
13. Lewis, J. B., *Chem. Eng. Sci.*, **3**, 248 (1954).
14. Lewis, J. B., I. Jones, and H. R. C. Pratt, *Trans. Inst. Chem. Engrs. (London)*, **29**, 126 (1951).
15. Markas, S. E. and R. B. Beckmann, *A.I.Ch.E. Journal*, **3**, 223, (1957).
16. Murphy, N. F., J. E. Lastovica, and A. E. Skrzec, *A.I.Ch.E. Journal*, **2**, 451 (1956).
17. Ruby, C. L., and J. C. Elgin, *Chem. Eng. Progr., Symposium Ser.*, No. 16, 17 (1955).
18. Wicks, C. E., and R. B. Beckmann, *A.I.Ch.E. Journal*, **1**, 426 (1955).

Manuscript received July 8, 1957; revision received Nov. 20, 1957; paper accepted Dec. 2, 1957.