Spray–extraction-tower Studies

A. I. JOHNSON, G. W. MINARD, CHEN-JUNG HUANG, J. H. HANSULD, and V. M. McNAMARA

University of Toronto, Toronto, Canada

This paper describes further research on a 4-in. I.D. by 8-ft. spray tower of Elgin design. Previous work concerned limiting flow and holdup in this tower. Owing to its high capacity and low cost, the spray tower would have much greater commercial application in liquid-liquid extraction if its conditions of transient operation could be predicted and if it could be operated to yield low H_t values. This research attempts to show that transient conditions can be predicted and that low H_t values for both mass and heat transfer can be realized near the limiting flow conditions.

Theoretical equations for rate of approach to steady state derived and tested for the systems ethylene dichloride–water–propionic acid and ethylene dichloride–water–acetic acid show that the approach depends on the ratio of the phase flow rates. This study is important for the prediction of start-up time for industrial towers.

With the same systems the extraction capacity of the spray tower was investigated up to the condition of rejection. The results were correlated as K_Ea and $H_{t,OE}$ vs. a function of the ratio of the phase flow rates. The dispersed-phase flow rate was found to have primary significance.

The heat transfer rates between water as continuous phase and solvents of various densities were correlated as H_t' values plotted against a function of the ratio of the phase flow rates. The advantages of operation near rejection were demonstrated, and the effect of direction of heat transfer was found to be significant.

Continuous extraction utilizes the countercurrent flow under the influence of gravity of the two phases in a vertical tower. In industry this has usually been carried out in packed, baffled, or sieve-plate towers. Spray towers, which have no packing and in which one phase passes through the second as drops, have been the subject of several investigations (*2, 3, 7, 8, 9, 12, 14, 16, 19, 20*). Such towers are inexpensive in construction and if operated near their flooding point have large throughputs and large interfacial areas.

This present discussion continues the first studies on the same apparatus, which were concerned with determining the conditions of flooding (*16*), and includes studies of the rate of approach to steady state along with extraction and heat transfer investigations. The studies were directed especially at operations near limiting flow conditions.

Since the experimental work in this paper was completed, two excellent researches have been reported (8, 9). Both of these were for a much smaller diameter column, 2 in., compared with 4 in. for the present study. The experimental results of the study on the rate of approach to steady state are believed to be the first for extraction operations.

APPARATUS

The apparatus has been discussed elsewhere in detail (*16*) and will be treated only briefly here, with reference to the flow diagram, Figure 1, and the column diagram, Figure 2.

The column was of Elgin design (*3*), which has been used extensively for recent spray- and packed-tower work. The main dimensions are shown in Figure 2. The column proper was an 8-ft. section of standard 4-in. Pyrex pipe. The flanges were machined from cast iron, then were heavily nickel plated. All piping and supply tanks were copper.

Although the tower may be easily

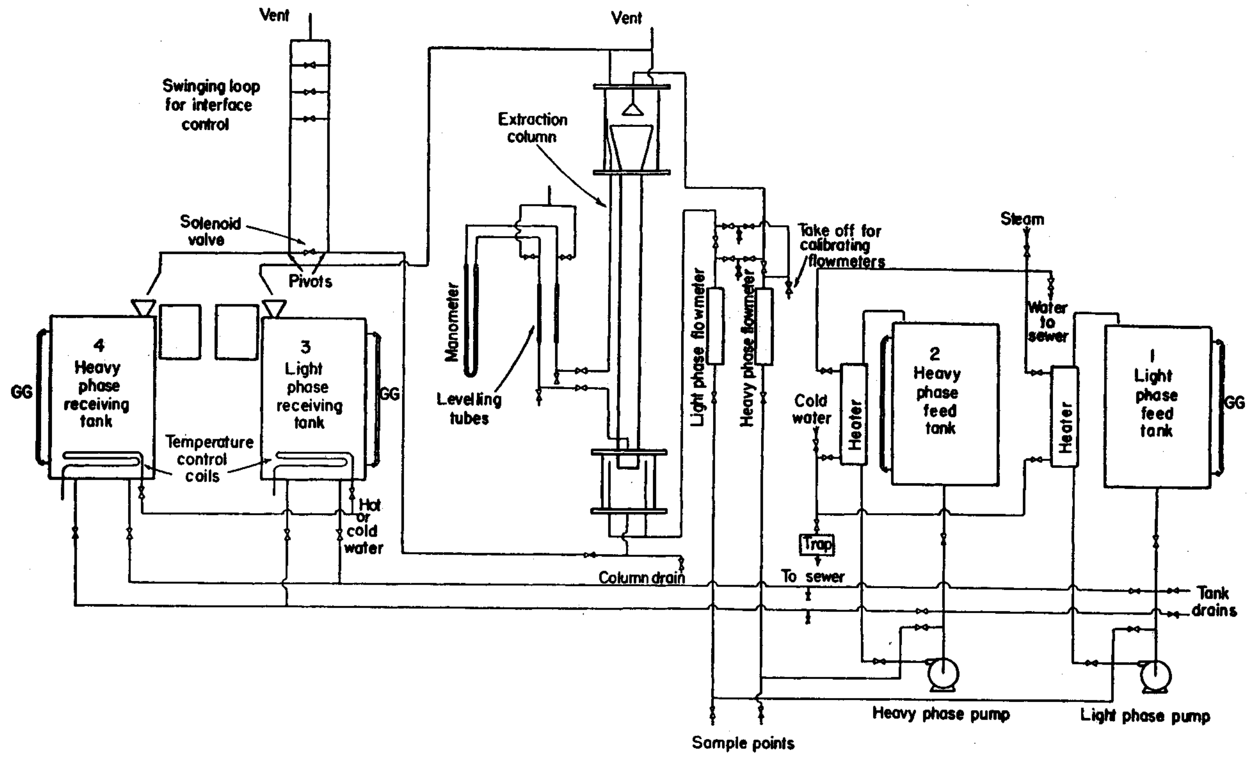

Fig. 1. Flow diagram for liquid-liquid–extraction apparatus spray-tower operation; heavy phase dispersed.

reversed, for all runs reported here the heavy phase was discontinuous. The dispersed phase enters through the spray nozzle in the upper spray section and enters the column proper through the conical entry piece. The drops of dispersed phase from the column proper settle in the lower chamber and are drawn off through the overflow loop. The continuous phase enters the column proper by means of the circular weir, passes countercurrent to the flow of dispersed phase, and overflows from the top of the column.

For studies of rate of approach to steady state and of mass transfer the feed and solvent solutions were made up in tanks 1 and 2, mixing and temperature adjustment being achieved by circulation of the liquid by the feed pumps through the small heat exchangers. The solutions were then pumped through the column at predetermined flow rates measured by the rotameters. The raffinate from the tower was collected in tank 4 and the extract was drained to the sewer. The unsteady state operation of the tower will be described in more detail later.

For the heat transfer studies tanks 3 and 4 were fitted with coils of ½-in. tubing. The heavy and light phases were circulated to and from these tanks where the heat exchanged in the column was added to or removed from the liquid as desired. The insulation and heating of the column for the heat transfer work are discussed in more detail later.

DEFINITION OF FLOODING AND REJECTION

In a spray tower of design similar to that used in this study the condition of flooding as originally defined by Elgin and Blanding (*3*) can be somewhat extended. Because there is a spray chamber and an entry cone of larger diameter than the tower proper, the bubbles of dispersed phase can entirely fill the entry cone and the tower will still operate smoothly even after flooding has occurred. On this basis Minard and Johnson (*16*) defined the absolute limiting flow as rejection, that condition at which the drops of dispersed phase overflow the entry cone into the annular space between the cone and the spray chamber. At this point the operation must be discontinued, as the annulus will soon fill with dispersed phase and eventually the drops will be prevented from forming properly at the spray nozzle or else they will pass off from the top of the tower with the continuous phase.

RATE OF APPROACH TO STEADY STATE

Most of the investigations in diffusional operations are concerned with the steady state condition, that is the condition when the operation of any equipment is independent of time. In any countercurrent mass transfer operation the initial concentrations of the exit streams will differ from the steady state conditions. The rate at which these concentrations approach the steady state conditions is of interest because in determinations of apparatus efficiency the operation must be continued long enough to allow initial variations to disappear before final measurements are taken. In some apparatus it may not be feasible to achieve fully steady state conditions and some means of predicting the final steady state conditions from the transient conditions may be desirable.

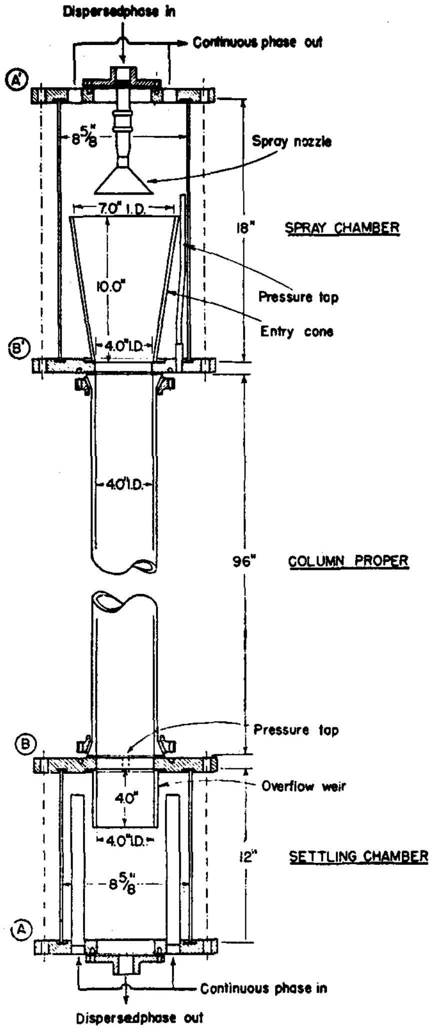

Fig. 2. Spray-extraction column; heavy phase dispersed.

The most advanced work in the field of unsteady state behavior in countercurrent operations has been done by Lapidus and Amundson (*13*), who considered the unsteady behavior of stagewise absorption and extraction equipment for both cross-current and countercurrent flow. Their treatment was entirely mathematical and no experimental data were presented. They assumed that the plate-type absorber was fed with a fat gas stream and a lean oil stream at a constant rate of the inert material and that the compositions of the entering streams to an absorber were functions of time. In other words, although the previous works were based on the constant compositions of the streams entering the tower, they considered the problems of unsteady feed concentrations. It was assumed further that initially any arbitrary composition can exist on the plate. Formulas were developed to show how the outgoing fat-gas and lean-oil compositions would vary with time. With these formulas, it is possible to compute the composition on any plate at any time for the countercurrent stagewise operation. A further mathematical treatment of transient behavior in stagewise operations which should be mentioned is that of Acrivos and Amundson (*1*).

The first part of the present study describes the development and testing of simpler formulas for differential continuous countercurrent extraction.

Theoretical Considerations

The method of attacking the problems involves first setting up simplified conditions which include the more important variables but disregard others and then applying material-balance equations. Since the terminal positions of the flows are fixed by the construction of the tower, it is apparent that the composition of the exit stream from a tower must be only a function of time. Flow rates of the two feed streams q_D for the dispersed phase and q_C for the continuous phase, in cubic feet per minute, will be considered to remain constant during the operation.

In order to simplify the problem, the time θ in minutes will be considered to be zero when the amount of the holdup of the dispersed phase in the column has reached a steady value. Then the amount of the holdup of the dispersed phase in the column will be constant during the operation because the flow rates are constant. Therefore any arbitrary compositions of the exit streams can exist initially because extraction has occurred to some extent during formation of the holdup in the column. It is assumed further that in this research the compositions of the two feed streams are invariable with time. As the mutual solubility between the solvent and the diluent is assumed to be zero, the amount of inert component in either the continuous or the dispersed stream is invariable in the process. Therefore the only variables with time are the concentrations of the two exit streams during the operation.

$C_{Ci}(\theta)$ and $C_{Di}(\theta)$ represent the time-dependent concentrations of the inlet continuous and dispersed phases, respectively, and $C_{CO}(\theta)$ and $C_{DO}(\theta)$ the equivalent concentrations in the outlet streams in pound moles of acid per cubic foot of phase at time (θ), minutes. As mentioned above, the concentrations of the inlet or outlet streams are functions of the time only. The continuous phase is the extract phase for the runs to be described.

The net inflow of the solute component to the column at the moment (θ) may be set equal to the rate of accumulation of the solute in the column. The resulting differential equation will be

$$q_D[C_{Di}(\theta) - C_{DO}(\theta)] + q_C[C_{Ci}(\theta) - C_{CO}(\theta)] = H\frac{d}{d\theta}[C_C(\theta)] + h\frac{d}{d\theta}[C_D(\theta)] \quad (1)$$

where H and h represent the steady state values of the holdup in the continuous and dispersed phases respectively, and $C_C(\theta)$ and $C_D(\theta)$ are the respective average column concentrations. In order to simplify the following equations all concentrations of either phase are to be read as transient concentrations; steady state values will be indicated as C'; initial values will be denoted as $C(0)$ with the appropriate subscript.

In order to relate the two dependent variables C_{DO} and C_{CO}, linear equilibrium relationships will be assumed at any moment; that is,

$$C_{CO} = \alpha C_{DO} + \beta \quad (2)$$

Similarly for the average concentrations,

$$C_C = \alpha C_D + \beta \quad (3)$$

These assumptions will result in the expression

$$q_D[C_{Di} - C_{DO}] + q_C[C_{Ci} - \alpha C_{DO} - \beta] = (H\alpha + h)\frac{d}{d\theta}[C_D] \quad (4)$$

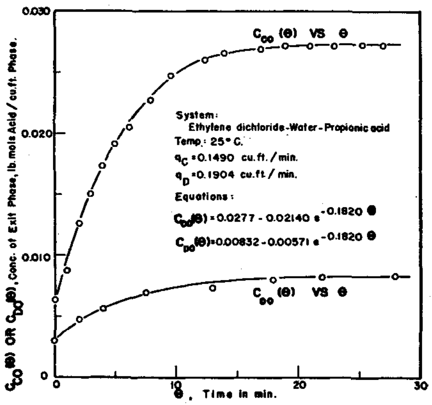

Fig. 3. Rate of approach to steady state.

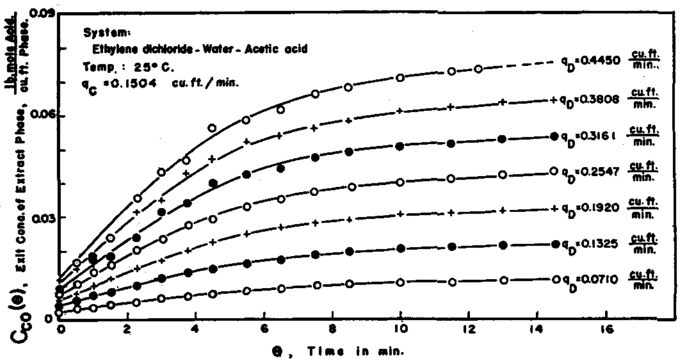

Fig. 4. Rate of approach to steady state.

Although the concentrations of the phases accumulated in the column are unknown, it has been assumed that the average concentration of each of these phases at any moment is a linear function of the instantaneous concentration of each exit stream from the tower. This may be expressed mathematically as

$$C_D = \gamma C_{DO} + \delta \quad (5)$$

$$C_C = \gamma C_{CO} + \delta \quad (6)$$

These assumptions will result in the expression

$$[q_D C_{Di}] + [q_C C_{Ci}] - [q_D C_{DO} + \alpha q_C C_{DO} + q_C\beta] = \gamma(H\alpha + h)\frac{d}{d\theta}[C_{DO}] \quad (7)$$

Substituting for the solute-free inlet concentration of continuous phase $C_{Ci} = 0$ reduces Equation (7) to a linear equation of the first order:

$$q_D C_{Di} - q_C\beta = [q_D + \alpha q_C]C_{DO} + \gamma(H\alpha + h)\frac{d}{d\theta}[C_{DO}] \quad (8)$$

This equation may be solved for C_{DO} thus:

$$C_{DO} = \left[\frac{q_D C_{Di} - q_C\beta}{q_D + q_C\alpha}\right] + [ke^{-B\theta}] \quad (9)$$

where $B = [(q_D + q_C\alpha)/(\gamma(H\theta + h))]$ and k is the integration constant.

The integration constant k can be evaluated when the value of C_{DO} is known at $\theta = 0$:

$$k = C_{DO}(0) - \left[\frac{q_D C_{Di} - q_C\beta}{q_D + q_C\alpha}\right] \quad (10)$$

Here $C_{DO}(0)$, the concentration of the exit dispersed phase at $\theta = 0$, can be determined either by experiment or by computation from the linear relationship:

$$C_{CO} = C_{DO} + \beta$$

when C_{CO} is measured. Therefore, Equation (9) will become

$$C_{DO} = \left[\frac{q_D C_{Di} - q_C\beta}{q_D + q_C\alpha}\right] + \left[C_{DO}(0) - \frac{q_D C_{Di} - q_C\beta}{q_D + q_C\alpha}\right]e^{-B\theta} \quad (11)$$

When operating conditions have reached steady state,

$$\frac{d}{d\theta}[C_{DO}] = 0 \text{ and } \frac{d}{d\theta}[C_{DO}] = 0 \quad (12)$$

Then C_{DO}', the concentration of the exit dispersed (raffinate) phase at steady state, will be calculated from Equation (1) by substitution of Equation (12):

$$q_D[C_{Di} - C_{DO}'] + q_C[C_{Ci} - C_{CO}'] = 0$$

and by use of Equation (3) with $C_{Ci} = 0$,

$$C_{DO}' = \frac{q_D C_{Ci} - q_C\beta}{q_D + q_C\alpha} \quad (13)$$

Introducing C_{DO} into Equation (11) gives

$$C_{DO}(\theta) = C_{DO}' + [C_{DO}(0) - C_{DO}']e^{-B\theta} \quad (14)$$

Therefore

$$C_{CO}(\theta) = \alpha C_{DO}' + \alpha[C_{DO}(0) - C_{DO}']e^{-B\theta} + \beta$$

$$C_{CO}(\theta) = C_{CO}' + [C_{CO}(0) - C_{CO}']e^{-B\theta} \quad (15)$$

where C_{CO}' is the concentration of the outlet continuous (extract) phase at steady state.

Equations (14) and (15) determine the concentrations of the exit streams at any moment under unsteady state conditions for the postulated differential continuous countercurrent extraction. As shown, these equations involve the relationship between the concentrations of the exit streams at any moment and their concentrations at steady state. Equation (13) shows that the concentration of the dispersed phase or the continuous phase at steady state varies with the flow rates of both streams. Then it may be concluded that the concentrations of the exit streams at any moment are influenced by the flow rates of both streams. Theoretically, these equations should be applicable right up to the limiting flow condition of the tower.

Method of Operation

The extraction tower system was operated as described in the general introduction for all the experimental runs made, the acid, either propionic or acetic, being extracted from an ethylene dichloride solution by means of water. The spray nozzle used had ninety-seven holes each 0.120 in. in diameter.

For most runs tanks 1 and 3 were filled with water, the temperature in tank 1 being adjusted to exactly 25°C. by the water circulating through the heat exchanger, and in tank 3 by the solenoid valve and temperature control coils installed in that tank. Both of these tanks were used as light phase feed to allow a longer run time at high flow rates to ensure that the desired steady state conditions would be attained. Tank 2 was filled with ethylene dichloride, recovered from the previous run in tank 4, and the acid was added until the desired concentration was attained.

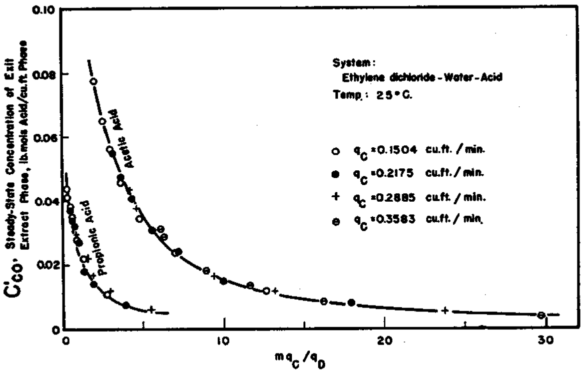

Fig. 5. Steady state concentration.

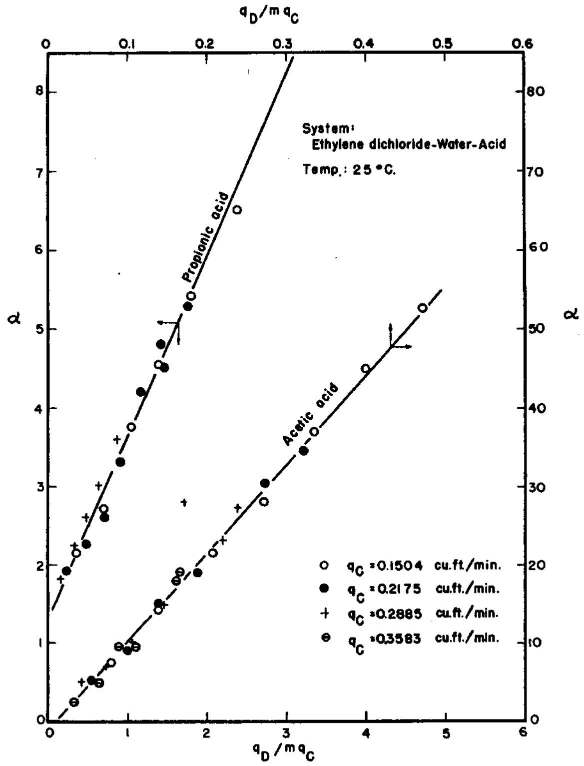

Fig. 6. Correlation of constant α.

The temperature of this solution was adjusted to 25°C. in a manner similar to that used for the water in the tank.

The run proper began by filling the tower with water, the flow rate being adjusted to the desired value and maintained constant at the flow meter. As soon as water began flowing from the top of the tower to the sewer, the heavy phase was pumped to the top of the tower, its predetermined flow rate being quickly attained and maintained constant. The dispersed phase settled at the bottom of the tower and when the interface level had risen to the 3-in. mark on the scale, the settled liquid was drawn off at the bottom at such a rate that the interface level remained constant.

When the amount of the holdup of the dispersed phase in the column had reached a constant value, the sampling of the exit phases was started and continued at regular intervals until the run was ended. When the mass transfer between phases had reached steady state, the run was deemed complete. The time to start taking the first samples was arbitrarily taken as the time when the pressure difference across the column reached a constant value, because the pressure difference was assumed to be due only to the dispersed-phase holdup in the tower proper (*16*). In most runs approximately 1 min. was required for the holdup of the dispersed phase to reach a steady value after the first drops left the spray nozzle.

As steady state conditions were approached, there was less fluctuation in the flow-meter readings and in the level of the interface, until finally the apparatus ran virtually by itself. Terminal compositions of the extract and raffinate phases were determined by manual sampling, titrations being carried out against standardized sodium hydroxide solution by use of phenolphthalein as the indicator.

For each set of runs made, a constant continuous-phase flow rate was selected. The lowest dispersed-phase flow rate used was 0.0710 cu. ft./min. and this rate was increased run by run until rejection occurred or until the run time was so short that steady state conditions could not be attained. The higher the continuous-phase flow rate used, the lower the dispersed-phase flow rate required for rejection to occur. As soon as rejection occurred for one constant continuous-phase flow rate, a new rate was selected and another set of runs begun.

Discussion of Results

Running Log of Exit Streams Concentrations. The concentrations of the exit phases plotted against time for Run III-B-3 are shown in Figure 3, and the data are given in Table 1.* This information is typical of the results obtained. At the beginning of the extraction operation the plot exhibits the general appearance of an exponential curve, but as steady state is attained the curve becomes asymptotic to some value on the ordinate axis. The time necessary to reach this certain value is theoretically

---

*Tabular material has been deposited as document 5120 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $3.75 for photoprints or $2.00 for 35-mm. microfilm.

infinite, as shown in Equations (14) and (15).

On the basis of the exit dispersed-phase composition, it requires about 6 min. to come within 5% of the steady state value. The equivalent time for the extract phase is 14 min. Before the concentration of the extract phase has reached a steady value, the concentration of the raffinate phase leaving the bottom of the settling chamber is approximately constant. This phenomenon can be explained by the fact that in the main body of the settled dispersed phase, mixing by convection and turbulence is so rapid that the concentration of the solute is essentially uniform at all points. Thus, although raffinate droplets of varying composition are continuously reaching the surface of the settled dispersed phase, there is negligible effect upon the concentration of the raffinate leaving the bottom of the tower. This is probably the reason for the shorter time of transient behavior in the raffinate phase as compared with the extract phase.

Figure 4 shows curves of $C_{CO}(\theta)$ vs. θ employing a continuous-phase flow rate of $q_C = 0.1504$ cu. ft./min. Each curve shows the transient behavior of the exit extract stream for a different flow rate of dispersed phase. For a constant flow rate of the continuous phase, the distance between the curves is proportional to the increase of the flow rate of the dispersed phase. The interval between any two adjoining curves is approximately constant because the flow rate of the dispersed phase was increased by the same amount for each run. When the operation approached flooding or rejection, the points deviated from the curve more than when the flow rate of the dispersed phase was low.

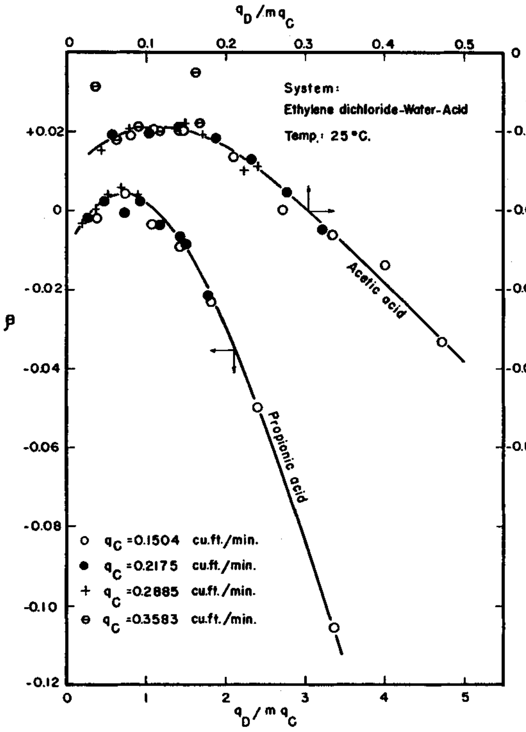

Fig. 7. Correlation of constant β.

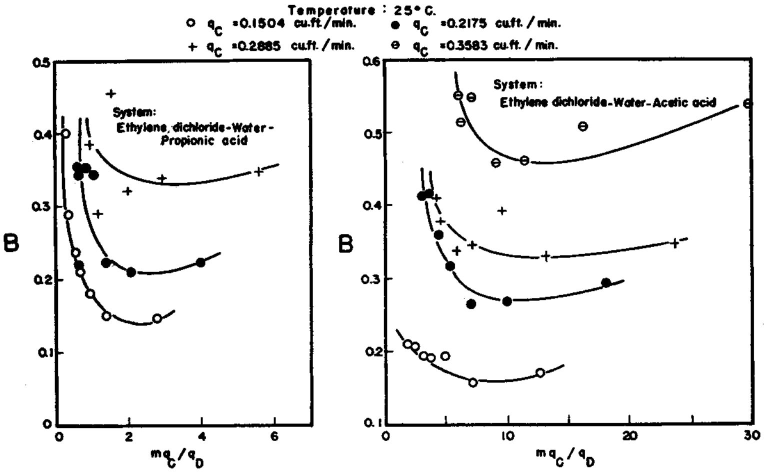

Fig. 8. Correlation of constant B.

Proposed Correlation of Results. General. There is no recognized way to correlate the experimental results under discussion. It is suggested, however, by analogy with relations developed for distillation and absorption that the constants α, β, and B in the theoretical equations and the steady state concentrations of exit phases C_{DO}, and C_{CO} can be correlated with the relation obtained by multiplication of the slope of the equilibrium distribution line and the flow ratio of the two phases: $m(q_C/q_D)$. The equilibrium distribution data for the systems employed in this research are presented in Table 2.

Steady State Exit Concentration of Extract Phase. The results shown in Figure 5 indicate that at steady state conditions the concentration of the exit continuous phase increases with increasing flow ratio of dispersed to continuous phases. The deviation of the observed value of the steady state concentration from that calculated from Equation (15) was within 5%. This implies the validity of the derived theoretical equations. The plot of C_{CO}' vs. $m(q_C/q_D)$ for both the systems studied as presented in Figure 5 produces a hyperbolic curve. From the graph the smaller the magnitude of the ratio $m(q_C/q_D)$ the higher will be the concentration of continuous phase leaving the top of the column. This concentration depends not upon the individual magnitudes of the flow rates but upon the relative ratio of the flow rates of the two phases. There is a practical limit to the individual values of q_C and q_D at the point of "rejection." Therefore it is suggested that the extraction operation should be carried out near this limiting flow condition with a low flow rate of continuous phase, in order to get a high concentration of exit continuous phase close to the equilibrium value C_{CO}.

Equation Constants. As originally postulated, Equations (14) and (15) are based on the assumption of a linear relation between the instantaneous concentrations of the extract and raffinate phases. A plot of $C_{CO}(\theta)$ against $C_{DO}(\theta)$ on ordinary coordinates produces an essentially straight line, an indication that the assumption is very nearly true. The constants α and β can then be determined by measuring the slope and intercept of the straight line. The constants so determined have been correlated for convenience with q_D/mq_C in Figures 6 and 7.

For the systems studied, the constant α bears a linear relation to the ratio q_D/mq_C. The magnitude of α is different for different systems owing to the fact that the equilibrium concentration of the extract phase for any fixed concentration of raffinate phase will be different.

On the other hand, the plot of β against q_D/mq_C on ordinary coordinates results in downward concave parabolic curves. In this case the constant has magnitudes specific for the system. At this stage both α and β can be evaluated only empirically.

Because of the difficulty of measuring the contact area, the holdup, and the concentrations of the phases at any moment in the column, the constant B in the derived equations could not be evaluated from these individual factors. Its value was obtained empirically by plotting $[C_{CO}' - C_{CO}(\theta)]$ against θ on semi-log coordinates. The slope of the resulting line is equal to the constant B, as could be deduced from Equation (15).

In all the curves shown on Figures 5, 6, and 7, individual flow rate was not an independent parameter. However, in the case of correlation of the constant B, flow rate does appear as a parameter, as is apparent in Figure 8, where the plots of B vs. mq_C/q_D give separate parabolic curves for each different dispersed-phase flow rate.

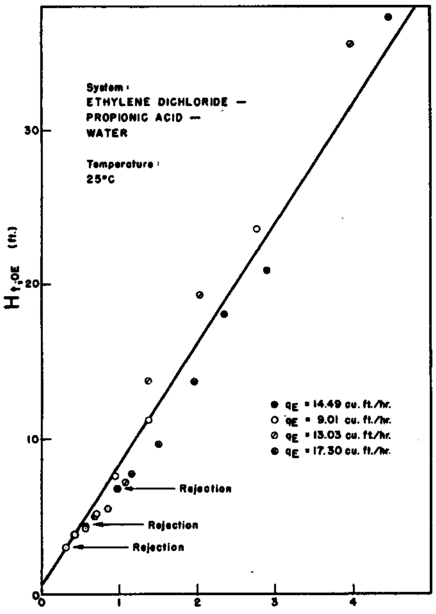

Fig. 9. Height-of-transfer-unit correlation.

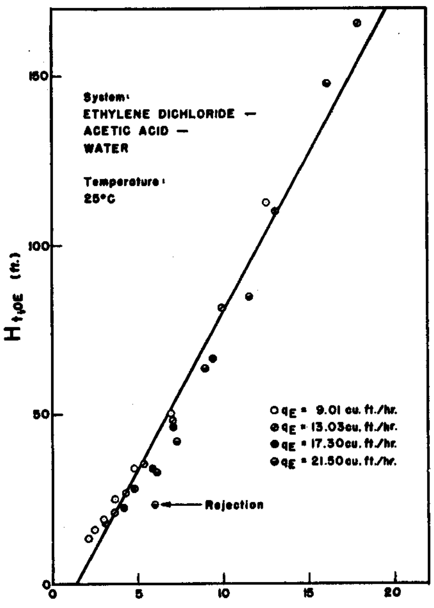

Fig. 10. Height-of-transfer-unit correlation.

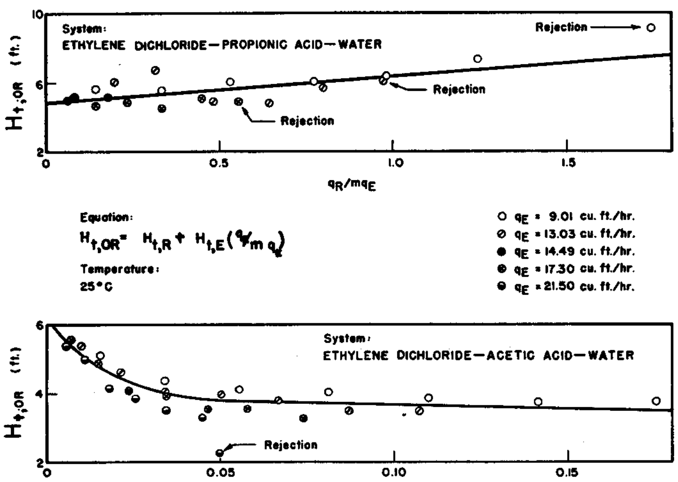

Fig. 11. Height-of-transfer-unit correlation.

Validity of Proposed Equations. The validity of the equations derived in this study is indicated in Table 1. Listed are the percentage deviations of each calculated concentration from the equation for the corresponding observed value for run III-B-3. The discrepancy between observed and calculated values was within 10%, which is acceptable for most engineering estimation. The numerical results of all runs are summarized in Tables 3 and 4.

It should be pointed out that the proposed equations are still valid even though an apparently large deviation from observed values occurs at high values of the time θ. This deviation exists because the ordinate values are the logarithms of the difference values $[C_{CO}' - C_{CO}(\theta)]$, and small experimental errors in either of the concentrations involved will result in large errors in the ordinate value.

Applications of the Equations. If the degree of approach to steady state is defined as ξ, the ratio of steady state concentration driving force to the instantaneous driving force, it may be expressed mathematically as

$$\xi = \frac{C_{CO}^* - C_{CO}'}{C_{CO}^* - C_{CO}(\theta)}$$

where C_{CO}^* represents the concentration of the exit continuous phase in equilibrium with the feed dispersed-phase concentration. Therefore, ξ can be evaluated analytically, by substitution of the equivalence of $C_{CO}(\theta)$ from the proposed Equation (15) into the foregoing expression.

MASS TRANSFER STUDIES

The results of several investigations of extraction capacities of spray columns have been reported (*2, 7, 8, 10, 11, 12, 15, 17*); however, except for the work of Fleming and Johnson (*8*), little emphasis has been placed on extraction near limiting flow conditions, where larger extraction coefficients would be expected owing to the greater surface area per unit volume and the greater turbulence in both phases. The purpose of this part of the present study was to investigate extraction coefficients, especially in the region of rejection.

Apparatus

The apparatus was the same as that discussed above. The runs reported here were carried out in conjunction with the unsteady state runs reported for the rate of approach to steady state.

Theory

The extraction results in this paper were correlated by use of both the transfer-unit concept and extraction coefficients. The transfer-unit concept for dilute solutions involves the defining equations suggested by Colburn (*4*):

Over-all number of transfer units based on extract phase

$$N_{t,OE} = \int_{C_{E_1}}^{C_{E_2}} \frac{dC_E}{(C_E^* - C_C)} \qquad (16)$$

Over-all height of a transfer unit based on extract phase

$$H_{t,OE} = \frac{Z}{(N_{t,OE})} \qquad (17)$$

Relation between over-all and film values of the heights of transfer units,

$$H_{t,OE} = H_{t,E} + H_{t,R}\left(\frac{mq_E}{q_R}\right) \qquad (18)$$

Graphic integration between the limits C_{E1} and C_{E2} in Equation (16) gives a value for $N_{t,OE}$ which when used in the relation of Equation (17) gives in turn a value of the over-all height of a transfer unit for the particular situation which gives the values of C_{E1} and C_{E2} used. Equation (18) may be used then to obtain the film values, as this relation represents a straight line when plotted with $H_{t,OE}$ as ordinate and mq_E/q_R as abscissa. The slope of this line will be $H_{t,R}$ and the ordinate intercept ($mq_E/q_R = 0$) will be $H_{t,E}$. Similar relations are available for the raffinate phase.

The value of m in Equation (18) may be determined by the exact method proposed by Colburn (*4*), which requires a time-consuming graphical integration across the entire tower height Z. The value of m may also be evaluated by use of the approximate method suggested by Duncan, Koffolt, and Withrow (*6*), which gives an integrated average value from the expression

$$m_a = \frac{\int_{C_{R_1}^*}^{C_{R_2}^*} m \, dC_R}{C_{R2}^* - C_{R1}^*} \qquad (19)$$

This is the value of m used in correlation of data in this present study. The value of m for use in Equation (18) may be evaluated by still another approximate method suggested by Colburn (*4*). Since the majority of transfer units are required in the dilute end of this countercurrent diffusional operation, a value of the slope of the distribution curve corresponding to C_{R1} is fairly accurate. For the specific case of a linear distribution curve all these methods reduce to equivalent expressions which are easily evaluated.

The mass transfer coefficient is related to the value of the H_t by the expression based on the extract phase

$$K_E a = q_E/(H_{t,OE})(S) \qquad (20)$$

A similar relation may be presented for the raffinate phase. In the present study the mass transfer coefficient data have been presented as a plot of the values of Ka for the continuous phase as ordinate against the flow velocity q/S of the dispersed phase.

Discussion of Results

Figures 9 and 10 illustrate the correlation of the data as $H_{t,OE}$ vs. the group mq_E/q_R. In general a straight-line relationship is observed as predicted by Equation (18). There is one obvious difference in the H_t data obtained for the systems studied. The plot in Figure 9 gives an ordinate intersection resulting in a positive value for $H_{t,E}$, which is to be expected. On the other hand, the plot in Figure 10 gives an unlikely negative value for $H_{t,E}$. This discrepancy indicates some limitation in this method of correlation. It should be pointed out, however, that this method correlates the particular data up to rejection.

Figure 11 shows $H_{t,OR}$ values correlated as a function of the group q_R/mq_E and shows that a satisfactory correlation of all the data was obtained up to the point of rejection; the curvature exhibited by the data for the system ethylene dichloride–acetic acid–water again indicates the limitation of the method.

Figures 12 and 13 show typical data for the systems involved plotted with extraction coefficient $K_E a$ as a function of the phase flow rates.

The main observation in these results is that normal operation up to the point of rejection was obtained. In general H_t values continued to decrease and $K_E a$ values continued to increase with increasing dispersed-phase flow rate for a given continuous-phase flow rate beyond Elgin flooding up the limiting flow condition described as rejection. No coalescence of the dispersed phase was observed in any of the runs made in this study.

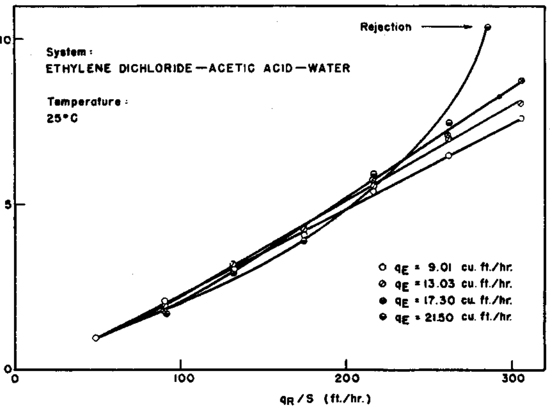

Fig. 12. Mass transfer coefficient correlation.

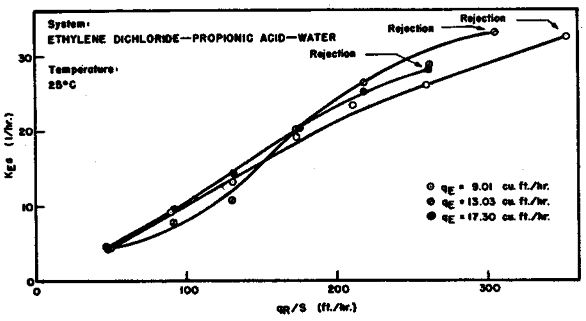

Fig. 13. Mass transfer coefficient correlation.

HEAT TRANSFER STUDIES

Extraction studies on a tower as large as the one used in this series of investigations can be carried out using many different systems only at considerable expense. In order to study the effect of varying physical properties of the solvent pairs on the operation of a spray column, it was decided to study the dynamically similar operation of extraction of heat. Preliminary heat transfer studies have been reported by Treybal (*20*) and by Garwin and Smith (*9*). This latter study used a single system and a 2-in.-diam. column.

Theoretical Principles

Equations for applying the transfer-unit concept to heat transfer may be set up in exactly the same manner as for mass transfer. For the over-all number of transfer units based on the continuous phase,

$$N_{t,OC}' = \int_{t_{C_1}}^{t_{C_2}} \frac{dt_C}{t_D - t_C} \qquad (21)$$

For dispersed phase,

$$N_{t,OD}' = \int_{t_{D_1}}^{t_{D_2}} \frac{dt_D}{t_D - t_C} \qquad (22)$$

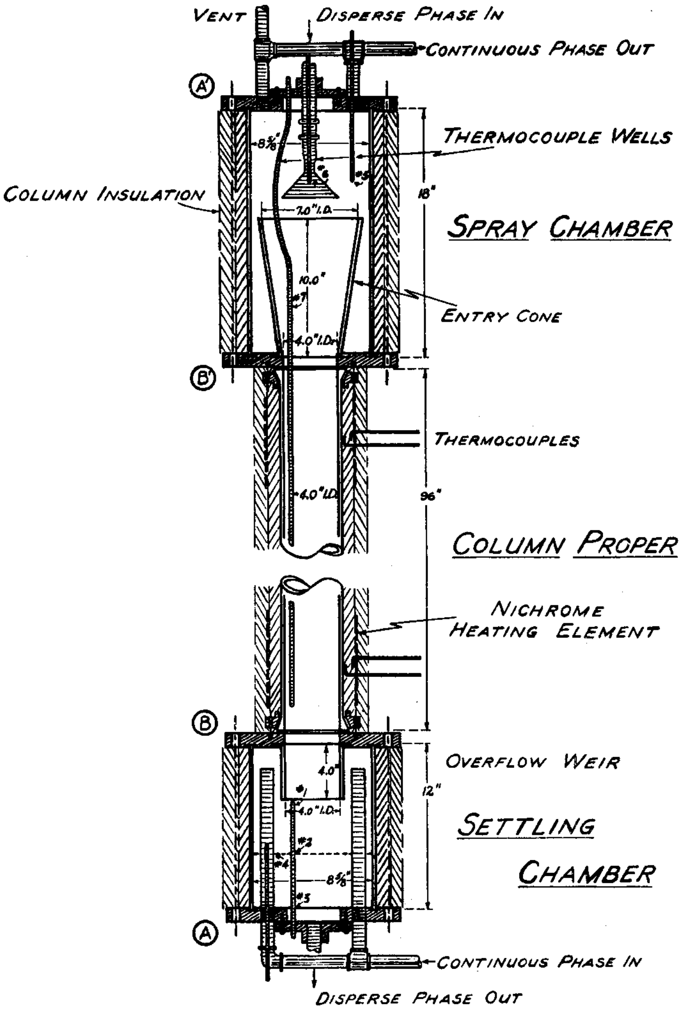

Fig. 14. Spray-tower; heavy phase dispersed.

For height of transfer unit,

$$H_t' = \frac{Z}{N_t'} \qquad (23)$$

Furthermore there is a similar relationship between the over-all and film values of H_t'. Therefore

$$H_{t,OC}' = H_{t,C}' + \left(\frac{V_C c_C}{V_D c_D}\right)(H_{t,D}') \qquad (24)$$

and

$$H_{t,OD}' = H_{t,D}' + \frac{V_D c_D}{V_C c_C}(H_{t,C}') \qquad (25)$$

In Equations (24) and (25) V_C and V_D are the continuous- and the dispersed-phase flow rates in cubic feet per hour per square foot and c_C and c_D are the respective heat capacities of the continuous and dispersed phases. The ratio of these latter variables is comparable to the slope of the equilibrium curve in mass transfer.

Since c_C and c_D may be assumed constant, the expression for N_t' may be simplified to

$$N_{t,OC}' = \frac{t_{C1} - t_{C2}}{(t_D - t_C)_{log\ mean}} \qquad (26)$$

Equations (23) to (26) were used for calculation and correlation in this part of the investigation.

Apparatus

The apparatus was essentially the same as shown in Figure 1. However, as indicated in Figure 14, the column was insulated by means of 2 in. of 85% magnesia-block insulation. The first inch of insulation on the column proper was wound with Nichrome heating wire, four turns to the inch, to form eleven separate heating circuits. Each heating circuit was controlled by a rheostat. A pair of thermocouples was installed at each heating circuit, one thermocouple touching the glass wall of the column and one just below the heating wire. The current to the heating wire was adjusted to maintain the column adiabatic.

Other thermocouples were placed in wells as indicated on Figure 14. These measured inlet and outlet temperatures of both phases. One long well extended through the column proper.

The two phases were recirculated to tanks 3 and 4, where copper heat exchange coils removed or returned the heat transferred in the column by circulation of cold or hot water inside the coils as required. Tanks 3 and 4 were also fitted with fume hoods to carry off fumes given off by the warm solutions.

Operation

The operation was very similar to that described by Minard and Johnson for flooding studies (*16*). For all runs the continuous phase was water. The dispersed phase consisted of carbon tetrachloride and carbon tetrachloride–naphtha mixtures. The properties of the mixtures are shown in Table 5. Either phase could be selected as the hot phase so that the transfer of heat in both directions was studied.

The continuous-phase flow rate was fixed, but the dispersed-phase flow rate was increased by small increments. About 1½ hr. were required for the temperature to become steady at each flow condition and for the column to become adiabatic. Thermocouple readings were taken and the dispersed-phase flow rate was again increased. This procedure was repeated until rejection was observed.

Two different spray heads were used. For most runs the nozzle used had twenty-one orifices 0.228 in. in diameter. Photographs of many of the runs were taken to record drop shape, size, and uniformity.

Discussion of Results

Figures 15, 16 and 17 illustrate typical results of the runs made in this part of the investigation. In general, runs were continued up to the point of rejection. This condition was chosen because it is easily reproduced and represents the highest possible throughput for the column. The terminal points on the plots represent rejection unless the run applying is starred; these runs were not carried beyond flooding.

The values of $H_{t,C}'$ decreased until rejection was attained, an indication that the most efficient operation of the tower corresponds to limiting flow conditions. No coalescence of drops was observed in any of the runs. It must be emphasized that no difference in drop size was observed between the two types of heat transfer operation.

The dispersed-phase rate at rejection for each continuous phase rate could be predicted with a maximum deviation of 15% by the original correlation of Minard and Johnson (*16*) an indication that those results hold for a wide range of temperatures of the phases and the resulting changes in physical properties.

The maximum hot-phase temperatures ranges from 126° to 140°F., higher temperatures causing excessive evolution of fumes.

Runs which gave heat balance differences greater than 10% were discarded.

Figure 18 shows the results of plotting $H_{t,D}'$ as a function of the ratio of the flow rates, V_D/V_C. These results are analogous and very similar to the results for $H_{t,OR}$ for extraction in the system ethylene dichloride–water–acetic acid shown in Figure 11. These curves show the influence of the direction of heat transfer on the observed results.

Figure 19 shows the results of all the runs for the three different solvent pairs used and for the two different nozzles. All calculated points fall along one or the other of a pair of parallel straight lines with a slope of approximately −1. The eight series of runs made in this investigation were analyzed by the method of least squares. This analysis also showed that if a normal allowance is considered for experimental error only, the direction of heat flow to or from the continuous phase was important in influencing the $H_{t,C}'$ values observed at a given V_D/V_C value.

The influence of direction of flow of heat or mass has been a controversial issue in recent years. It is believed that these results demonstrate rather conclusively that an effect of direction of heat transfer does exist. If the continuous phase can be said to have the controlling resistance as indicated by the high $H_{t,C}'$ values observed and correlated in Figure (19), then this effect could be explained qualitatively as being due to the lower viscosity of the continuous phase in the continuous-phase film near the drop. The heat transfer coefficient would be increased when the dispersed phase was hot and decreased when the dispersed phase was cold. This effect appears similar to the wall correction factor used to correlate heat transfer coefficients for fluids flowing in pipes, introduced by Sieder and Tate (*18*).

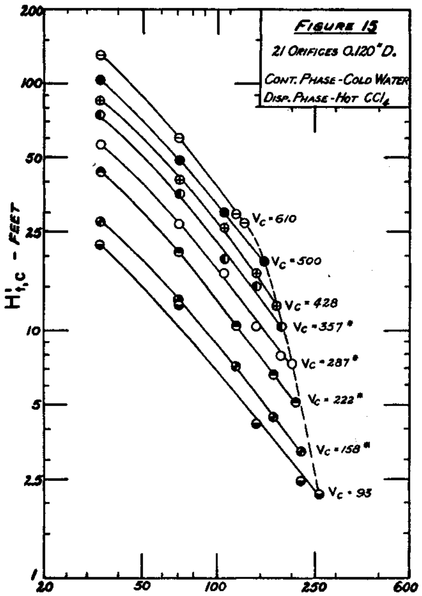

Fig. 15. Twenty-one orifices 0.120-in. diam.; continuous phase, cold water; dispersed phase, hot CCl₄.

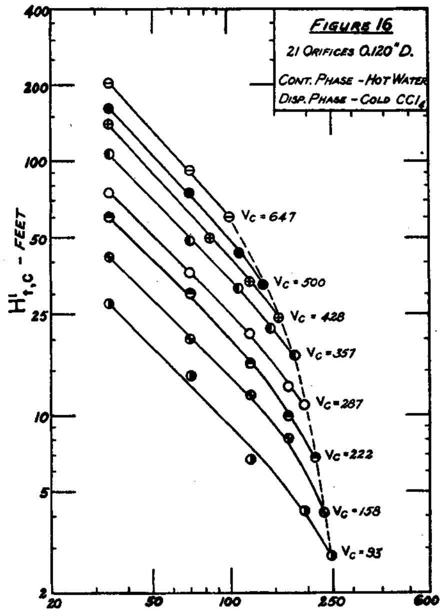

Fig. 16. Twenty-one orifices 0.120-in. diam.; continuous phase, hot water; dispersed phase, cold CCl₄.

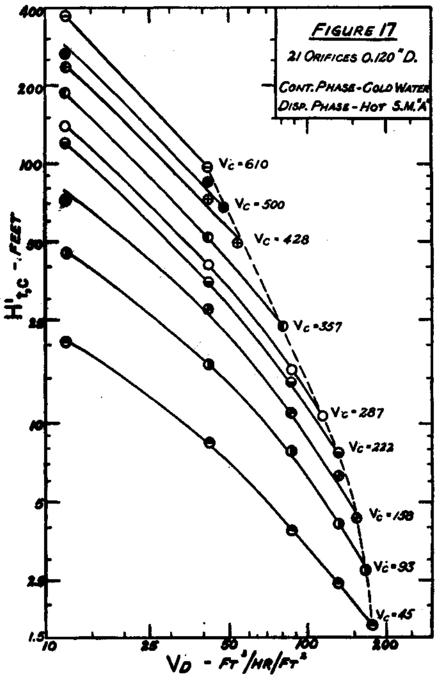

Fig. 17. Twenty-one orifices 0.120-in. diam.; continuous phase, cold water; dispersed phase, hot S.M."A".

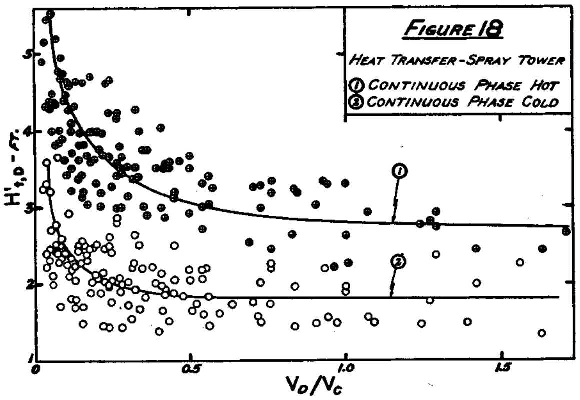

Fig. 18. Heat transfer, spray tower; (1) continuous phase hot, (2) continuous phase cold.

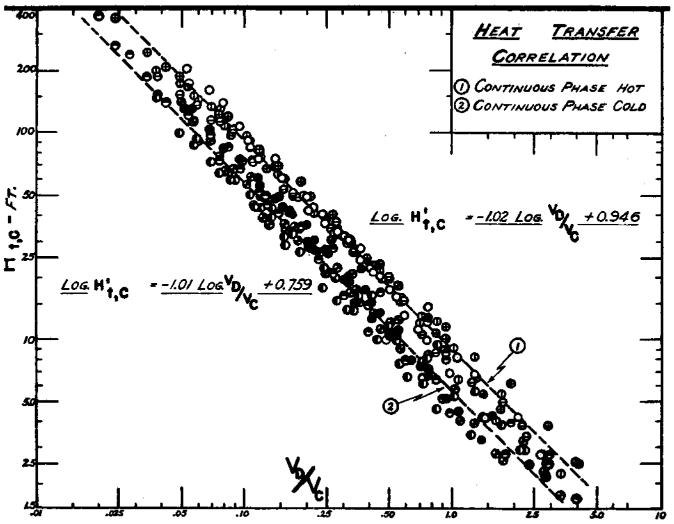

Fig. 19. Heat transfer correlation; (1) continuous phase hot, (2) continuous phase cold.

Perhaps a more plausible explanation stems from the work of Conkie and Savic (*5*), who showed theoretically that the coefficient for heat transfer from drops should vary as the ratio of the heat transfer coefficient for the boundary layer of the surrounding film to the viscosity of the droplet fluid. If the conditions of turbulence of the drops and the continuous phase in the present investigation agree with the conditions set up in the theory of Conkie and Savic, and this seems likely, then it would be expected that the heat transfer coefficient would be greater when the continuous phase is cold, as was observed.

These explanations, of course, require further examination and further experimental measurements.

CONCLUDING REMARKS

This investigation has attempted to present in concise form an intensive study of the rate of approach to steady state in extraction, mass transfer in extraction, and rate of heat transfer in an Elgin type of spray tower. Combined with the previous study of holdup and limiting flow, this series of investigations permits a more thorough understanding and prediction of spray-tower behavior.

The results are all for a 4-in.-diam. tower giving a large ratio of tower diameter to drop size. The results on the rate of approach to steady state are believed to be the first reported for a spray tower. The simplified equations proposed for transient conditions permit extrapolation to steady state conditions. The constants required in these equations may be correlated as functions of the ratio of the flow rates of the two phases. This ratio is also the most useful quantity for correlating mass transfer and heat transfer data.

During extraction the tower was shown to give stable operation up to and beyond flooding conditions. The H_t values continue to decrease for any given continuous-phase rate as the limiting flow condition is approached, including operation up to rejection. Results are presented for two systems not previously studied.

The heat transfer data show the advantages of using the transfer of heat rather than transfer of mass to study tower performance. Over rather wide ranges of operating conditions, no influence of the density of the dispersed phase was observed. The effect of changing drop size was small; however, the effect of the direction of heat flow was pronounced. Tentative explanations for this effect are suggested, but further study of this phase of work is required.

NOTATION

B = correlating parameter
c = specific heat, B.t.u./(lb.)(°F.)
C' = steady state solute concentration, lb.-moles/cu. ft.
$C(\theta)$ = time-dependent solute concentration, lb.-moles/cu. ft.
C^* = equilibrium solute concentration, lb.-moles/cu. ft.
h = absolute holdup of dispersed phase, cu. ft.
H = absolute holdup of continuous phase, cu. ft.
H_t = height of transfer unit–mass transfer, ft.
H_t' = height of transfer unit–heat transfer, ft.
k = integration constant
Ka = volumetric mass transfer coefficient, 1/hr.
m = slope of equilibrium distribution curve
N_t = number of transfer units–mass transfer
N_t' = number of transfer units–heat transfer
q = flow rate, cu. ft./min. or cu. ft./hr. as indicated
S = cross-sectional area of column proper, sq. ft.
t = temperature, °F.
V = phase flow rate, cu. ft./(hr.)(sq. ft.)
Z = height of column, ft.
$\alpha, \beta, \gamma, \delta$ = correlating parameters
θ = time, min.
ξ = degree of approach to steady state

Subscripts

a = average value
C = continuous phase
D = dispersed phase
E = extract phase
i = inlet to column
o = outlet from column
O = over-all value
R = raffinate phase
1 = inlet condition of phase
2 = outlet condition of phase

LITERATURE CITED

1. Acrivos, Andrew, N. R. Amundson, *Ind. Eng. Chem.*, **47**, 467 (1953).
2. Appel, F. J., and J. C. Elgin, *ibid.*, **29**, 451 (1937).
3. Blanding, F. H., and J. C. Elgin, *Trans. Am. Inst. Chem. Engrs.*, **38**, 305 (1942).
4. Colburn, A. P., *ibid.*, **35**, 211 (1939).
5. Conkie, W. R., and P. Savic, *Rept.* MT23, Natl. Research Council Canada (October, 1953).
6. Duncan, D. W., J. H. Koffolt, and J. R. Withrow, *Trans. Am. Inst. Chem. Engrs.*, **38**, 259 (1942).
7. Elgin, J. C., and F. M. Browning, *ibid.*, **31**, 639 (1935).
8. Fleming, J. F., and H. F. Johnson, *Chem. Eng. Progr.*, **49**, 497 (1953).
9. Garwin, Leo, and B. D. Smith, *Chem. Eng. Progr.*, **49**, 591 (1953).
10. Geankoplis, C. J., and A. N. Hixson, *Ind. Eng. Chem.*, **42**, 1141 (1950).
11. Hayworth, C. B., and R. E. Treybal, *ibid.*, **42**, 1174 (1950).
12. Johnson, H. F., and Harding Bliss, *Trans. Am. Inst. Chem. Engrs.*, **42**, 331 (1946).
13. Lapidus, Leon, and N. R. Amundson, *Ind. Eng. Chem.*, **42**, 1071 (1950).
14. Licht, William, and J. B. Conway, *ibid.*, **42**, 1151 (1950).
15. Meissner, H. P., C. A. Stokes, C. M. Hunter, and G. M. Morrow, *ibid.*, **36**, 917 (1944).
16. Minard, G. W., and A. I. Johnson, *Chem. Eng. Progr.*, **48**, 62 (1952).
17. Row, S. B., J. H. Koffolt, and J. R. Withrow, *Trans. Am. Inst. Chem. Engrs.*, **37**, 559 (1941).
18. Sieder, E. N., and G. E. Tate, *Ind. Eng. Chem.*, **28**, 1429 (1936).
19. Sherwood, T. K., J. E. Evans, and J. V. A. Longcor, *ibid.*, **31**, 1144 (1939).
20. Treybal, R. E., "Liquid Extraction," McGraw-Hill Book Company, Inc., New York (1951).