

- Ω_2 = dimensionless flow reversal viscous drag force:
 $(3/8)^{1/2} K_T r_o \mu / (\rho g^{1/2})$
 Ω_3 = dimensionless surface tension: $K_{ST}(\cos \phi_R - \cos \phi_A) / (r_o^2 \rho g)$
 $\langle \rangle$ = quantity averaged over area of tube
 ρ = fluid density, g./cc.

LITERATURE CITED

1. Bird, R. B., W. E. Stewart, and E. N. Lightfoot, "Transport Phenomena," 1 ed., pp. 229-231, Wiley, New York (1961).
2. Ceaglske, N. H., "Automatic Process Control for Chemical Engineers," 1 ed., pp. 75-76, Wiley, New York (1956).
3. Miller, G. E., "Transient State Flow of a Non-Newtonian Fluid," unpublished report, Univ. of Texas, Austin, Texas (1960).
4. Martin, R. J., and D. S. Moseley, *Trans. Am. Soc. Mech. Engrs.*, **80**, 1343-8 (1958).
5. Williams, T. J., *Trans. Am. Soc. Mech. Engrs.*, **78**, 1461-9 (1956).
6. McKennell, Raymond, "Proc. 2nd Intern. Congr. Rheol. 1953," p. 350, Butterworth's, London, England (1954).
7. Biery, J. C., and J. D. Huppler, "Newtonian and Non-Newtonian Viscosity Determinations on a Cone and Plate Viscometer," *Engineering Experiment Station Report No. 19*, Univ. of Wisconsin, Madison, Wisconsin (1962).
8. Hodgman, C. D., R. C. Weast, and M. S. Selby, editors, "Handbook of Chemistry and Physics," 42 ed., The Chemical Rubber Publishing Co., Cleveland, Ohio (1961).
9. Snedecor, G. W., "Statistical Methods," 5 ed., The Iowa State College Press, Ames, Iowa (1956).
10. Savant, C. J. Jr., "Basic Feedback Control System Design," 1 ed., p. 9, McGraw-Hill, New York (1958).
11. Hildebrand, F. B., "Introduction to Numerical Analysis," 1 ed., p. 75, McGraw-Hill, New York (1956).
12. Lamb, H., "Hydrodynamics," 6 ed., p. 622, Dover Publications, New York (1932).
13. Goldstein, S., ed., "Modern Developments in Fluid Dynamics," Vol. 1, pp. 312-314, Oxford Press, London, England (1950).

Manuscript received November 1, 1962; revision received March 1, 1963; paper accepted March 5, 1963.

The Dynamic Behavior of a Pulsed-Plate Extraction Column

JOHN W. WATJEN and ROBERT M. HUBBARD

University of Virginia, Charlottesville, Virginia

To achieve better design of automatically controlled systems, there is an increasing need to determine experimental data describing the dynamic behavior of chemical process equipment. Some few data have been published for countercurrent diffusional operations such as absorption (1, 3, 4) and extraction columns. Recently two papers (2, 7) have appeared describing the dynamic behavior of pulse-plate extraction columns based on both analog and digital computer solutions of mathematical models. The present work was undertaken to provide experimental dynamic extraction data to compare with linear theoretical models over the entire range of column flow conditions.

A pulsed-plate extraction column was chosen for the experimental work because variation of the column pulsation frequency allowed collection of data over a large range of mass transfer efficiency and fluid turbulence. The dynamic response of the system was measured with and without mass transfer to determine the effect of fluid flow on the overall column dynamics.

The theoretical linear-model response was determined by writing the general time-dependent differential material-balance equation for a model with mass transfer and fluid mixing and by solving the equivalent finite-difference equation using Laplace transforms. The solution gave the output as a function of signal frequency ($s = j\omega$) when the system was initially disturbed by a specific input such as a unit step or a pulse. At each value of signal frequency these results were expressed as the ratio of output-to-input amplitude (magnitude) and as the phase difference between the input and output.

At four column-pulsation frequencies, the experimental dynamic response was determined by the pulse method (5) for conditions of good mass transfer and of no mass transfer. The combined response was determined with a pulse of acid into the methyl isobutyl ketone, acetic acid, water system. The fluid-flow response was determined with a pulse of scarlet-red dye, which was insoluble in the methyl isobutyl ketone phase. The acid concentration was measured by titrating output samples, and the dye concentration was measured with a spectrophotometer. The flow rates, mass transfer stage efficiencies, and eddy

John W. Watjen is with E. I. DuPont de Nemours and Company, Incorporated, Wilmington, Delaware.

diffusivities, as well as the column holdup in the aqueous and solvent phases, were also determined at each value of the column-pulsation frequency.

THEORETICAL METHOD

Figure 1 shows the differential element, dZ , of a continuous vertical contacting column. The following assumptions for the contacting of the two liquid phases in the column were made.

1. Within the narrow range of concentration used experimentally, the aqueous flow rate, the solvent flow rate, the equilibrium distribution coefficient, and the product of the mass transfer coefficient and the interfacial area per unit column volume were constant.

2. The gradient of solute concentration in each phase was continuous.

3. The mean velocity and concentration of each phase were constant across that part of the column cross section occupied by the phase. Thus the concentration gradients existed only in the direction of flow.

4. The effect of pulsation of the material in the column was described by backmixing of the fluid with a constant axial eddy diffusivity coefficient.

5. The approach to mass transfer equilibrium within the column was characterized by an overall liquid efficiency.

For a unit cross section of column, an overall acid material balance is

$$-L \frac{\partial x}{\partial Z} + G \frac{\partial y}{\partial Z} + e_L D_{LA} \frac{\partial^2 x}{\partial Z^2} + e_G D_{GA} \frac{\partial^2 y}{\partial Z^2} = h' \frac{\partial x}{\partial t} + H' \frac{\partial y}{\partial t} \quad (1)$$

If assumptions 2 and 5 are replaced, respectively, by (2a) the gradient of solute concentration in each phase is composed of finite steps associated with the area between two successive plates, and (5a) the approach to mass transfer equilibrium within the area between two successive plates is characterized by a liquid plate or stage efficiency, Equation (1) can be approximated in the finite difference form as

$$L(x_{m-1} - x_m) + G(y_{m+1} - y_m) + \frac{e_G D_{GA}}{n \Delta Z} (y_{m+1} - 2y_m + y_{m-1}) + \frac{e_L D_{LA}}{n \Delta Z} (x_{m-1} - 2x_m + x_{m+1}) = h \frac{dx_m}{dt} + H \frac{dy_m}{dt} \quad (2)$$

The equilibrium relation is

$$x_m^* = \frac{y_m}{r} \quad (3)$$

and the liquid stage efficiency is defined as

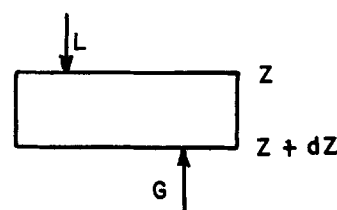
$$E_m = \frac{x_m - x_{m-1}}{x_m^* - x_{m-1}} \quad (4)$$

When Equation (3) is substituted into Equation (4) one obtains

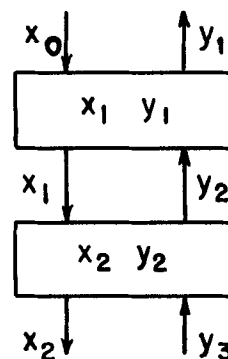
$$y_m = \frac{r x_m}{E_m} - \frac{r(1 - E_m)}{E_m} x_{m-1} \quad (5)$$

Substituting Equation (5) into Equation (2) gives

$$\left[\frac{rG}{E_m} + \frac{re_G D_{GA}}{n \Delta Z E_m} + \frac{e_L D_{LA}}{n \Delta Z} \right] x_{m+1} - \left[L + \frac{rG}{E_m} + \frac{re_G D_{GA}}{n \Delta Z E_m} (1 - E_m) + \frac{rG}{E_m} (1 - E_m) + \frac{2re_G D_{GA}}{n \Delta Z E_m} + \frac{2e_L D_{LA}}{n \Delta Z} \right] x_m + \left[L + \frac{rG}{E_m} (1 - E_m) + \right.$$



DIFFERENTIAL ELEMENT



FINITE DIFFERENCE ELEMENT

Fig. 1. Theoretical model of elements of extraction column.

$$\frac{2re_G D_{GA}}{n \Delta Z E_m} (1 - E_m) + \frac{re_G D_{GA}}{n \Delta Z E_m} + \frac{e_L D_{LA}}{n \Delta Z} \Big] x_{m-1} - \left[\frac{re_G D_{GA}}{n \Delta Z E_m} (1 - E_m) \right] x_{m-2} = \left[h + \frac{rH}{E_m} \right] \frac{dx_m}{dt} - \frac{rH}{E_m} (1 - E_m) \frac{dx_{m-1}}{dt} \quad (6)$$

The acid concentration is the sum of a steady state value plus a transient, defined as

$$x = \bar{x} + x' \quad (7)$$

The steady state portion of Equation (6) can be subtracted from the total expression, leaving only the dynamic portion. When a two-plate column (Figure 1) is excited by a unit step change in aqueous phase, the boundary conditions for $x_m(t)$ and $y_m(t)$ are

- (a) $x_m'(0) = y_m'(0) = 0$ for $m \neq 0$
- (b) $y_3'(0) = 0$
- (c) $x_0'(0) = U(t) = 1$ and, when Laplace transformed, $x_0'(s) = 1/s$

Thus for the first finite stage, Equation (6) becomes

$$\left[\frac{rG}{E_2} + \frac{re_G D_{GA}}{n \Delta Z E_2} + \frac{e_L D_{LA}}{n \Delta Z} \right] x_2' - \left[L + \frac{rG}{E_2} (1 - E_2) + \frac{rG}{E_1} + \frac{re_G D_{GA}}{n \Delta Z E_2} (1 - E_2) + \frac{2re_G D_{GA}}{n \Delta Z E_1} + \frac{2e_L D_{LA}}{n \Delta Z} \right] x_1' + \left[L + \frac{rG}{E_1} (1 - E_1) + \frac{2re_G D_{GA}}{n \Delta Z E_1} (1 - E_1) + \frac{e_L D_{LA}}{n \Delta Z} \right] x_0' = \left[h + \frac{rH}{E_1} \right] \frac{dx_1'}{dt} \quad (8)$$

The Laplace transform of Equation (8) with respect to time is

$$x_1'(s) = \frac{I_1 x_2'(s) + I_2 \frac{1}{s}}{I_3 + I_4 s} \quad (9)$$

where

I_1 = coefficient of x_2' in Equation (8)

I_2 = coefficient of x_0' in Equation (8)

I_3 = the absolute value of the coefficient of x_1' in

Equation (8), and

I_4 = coefficient of dx_1'/dt in Equation (8)

A similar Equation (8) for the second stage is

$$x_1'(s) = \frac{(I_5 + I_6 s) x_2'(s) + I_7 \frac{1}{s}}{I_8 + I_9 s} \quad (10)$$

where

$$I_5 = L + \frac{rG}{E_2} + \frac{2regDGA}{n \Delta Z E_2} + \frac{2eLDLA}{n \Delta Z}$$

$$I_6 = h + \frac{rH}{E_2}$$

$$I_7 = \frac{regDGA}{n \Delta Z E_1} (1 - E_1)$$

$$I_8 = L + \frac{rG}{E_2} (1 - E_2) +$$

$$\frac{2regDGA}{n \Delta Z E_2} (1 - E_2) + \frac{regDGA}{n \Delta Z E_1} + \frac{eLDLA}{n \Delta Z}$$

$$I_9 = \frac{rH}{E_2} (1 - E_2)$$

When Equations (9) and (10) are equated and the result is solved for $x_2'(s)$, the transfer function is

$$\text{T.F.} = \frac{x_2'(s)}{x_0'(s)} = \frac{(I_2 I_8 - I_3 I_7) + (I_2 I_9 - I_4 I_7) s}{I_4 I_6 s^2 + (I_3 I_6 + I_4 I_5 - I_1 I_9) s + (I_3 I_5 - I_1 I_8)} \quad (11)$$

This same method of solution can be used for a column with any number of plates. The general transfer function is

$$\text{T.F.} = \frac{x_m'(s)}{x_0'(s)} = K \frac{\prod_{i=1}^{i=m-1} (T_i s + 1)}{\prod_{i=m}^{i=2m-1} (T_i s + 1)} \quad (12)$$

When Equations (11) and (12) are solved for the special case of no mass transfer, Equation (11) becomes

$$\text{T.F.} = \frac{x_2'(s)}{x_0'(s)} = \frac{\left(L + \frac{eLDLA}{n \Delta Z} \right)^2}{\left[hs + \left(L + \frac{2eLDLA}{n \Delta Z} \right) \right]^2 - \frac{eLDLA}{n \Delta Z} \left(L + \frac{eLDLA}{n \Delta Z} \right)} \quad (13)$$

The general transfer function is

$$\text{T.F.} = \frac{x_m'(s)}{x_0'(s)} = \frac{K}{\prod_{i=1}^{i=m} (T_i s + 1)} \quad (14)$$

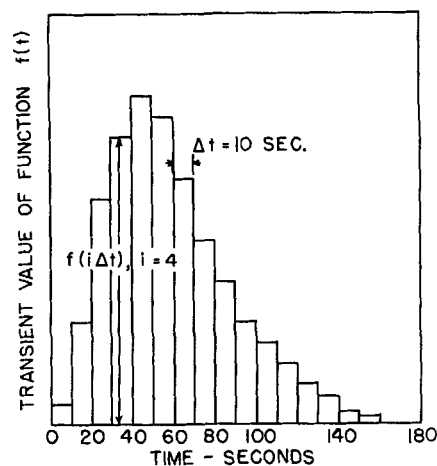


Fig. 2. Typical experimental dynamic response function.

PULSE METHOD OF DYNAMIC ANALYSIS

Recently the pulse-response method has been used by Hougen (5) in the dynamic analysis of chemical systems. In frequency-response analysis the data are obtained after all transient response has disappeared. However, the pulse method analyzes the transient response of a system to an upset in an input variable. During a transient response the system response exists at all frequencies simultaneously. One experiment, therefore, replaces all those required by the frequency-response method, although analysis of the data is more complicated.

A pulse is a function which differs from zero or some other reference value for only a finite time (5). The pulse does not need to correspond to any definite mathematical form, and if its duration is small compared with the duration of the response, a mathematical form which the experimental pulse approximates can be used for calculation. The main experimental requirement is that the pulse be large enough to excite the system dynamics without causing nonlinearities such as flooding. Thus the extraction column in the present work was excited by a pulse large enough to give an output response which could be determined accurately, but small enough to leave the flow characteristics in the column essentially undisturbed or nearly linear.

A pulse function, such as the rectangular input pulse used in the present work, is Laplace transformable (4). The Laplace transform of the function can be represented as

$$L[f(t)] = \int_0^{\infty} f(t) e^{-st} dt \quad (15)$$

When a stable system is excited by an input pulse, its output varies in a pulslike manner. If both pulses are transformed, the resulting transfer function is

$$\text{T.F.} = \frac{L[f_{\text{out}}(t)]}{L[f_{\text{in}}(t)]} = \frac{M_{\text{out}}(j\omega)}{M_{\text{in}}(j\omega)} e^{-j(\theta_{\text{out}} - \theta_{\text{in}})\omega} \quad (16)$$

The Laplace transform of the experimental output response was approximated from data similar to that shown in Figure 2 by use of the equation

$$L[f_{\text{out}}(t)] = \sum_{i=1}^{i=J} f_{\text{out}}(i\Delta t) \cos(\omega_i \Delta t) \Delta t - j \sum_{i=1}^{i=J} f_{\text{out}}(i\Delta t) \sin(\omega_i \Delta t) \Delta t \quad (17)$$

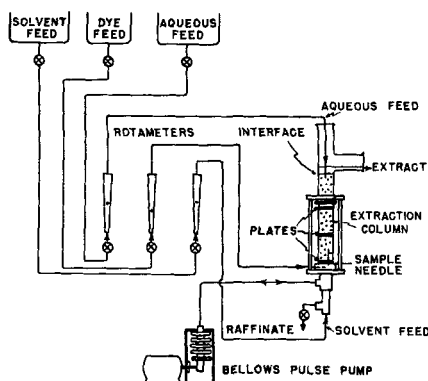


Fig. 3. Schematic diagram of experimental extraction system.

The sum of the cosine terms gave the real part of the complex function and the sum of the sine terms the imaginary part. Thus the magnitude of the output was

$$M_{out} =$$

$$\sqrt{(\text{sum of cosine terms})^2_{out} + (\text{sum of sine terms})^2_{out}}$$

and the phase angle was

$$\theta_{out} = \tan^{-1} \left(- \frac{\text{sum of the sine terms}}{\text{sum of the cosine terms}} \right)$$

In the present work the short-interval input pulse was assumed rectangular. Thus there was only one interval, $i = 1$, and Equation (17) applied to the input became

$$L[f_{in}(t)] = f_{in}(\Delta t_{in}) [\cos(\omega \Delta t_{in}) - j \sin(\omega \Delta t_{in})] \Delta t_{in}$$

The magnitude of the input function was

$$M_{in} = f_{in}(\Delta t_{in}) \Delta t_{in}$$

and the phase angle was

$$\theta_{in} = -\omega \Delta t_{in}$$

The magnitude of the transfer function was

$$M = \frac{M_{out}}{M_{in}}$$

and the phase angle was

$$\theta = \theta_{out} - \theta_{in}$$

EXPERIMENTAL

Equipment

The dynamic studies were made in $\frac{3}{4}$ -in. I.D. uniform-bore glass columns (Figure 3) with two or three plates. The sieve plates were held 2 in. apart. Each plate was 28-gauge stainless steel with ninety-nine 0.04-in.-diam. holes and 28% free area for flow. The top section of the column was a standard $\frac{3}{4}$ -in. Pyrex glass tee which allowed the top interface in the column to be held 2 in. above the top plate with minimum solvent holdup above the interface. The holdup in the bottom section was negligible.

The liquid in the column was pulsed by a variable-speed bellows pump without valves connected to the bottom section of the column. Column pulse amplitude was 4 mm. Pump pulsation frequencies from approximately 25 to 40 cycles/min. caused mixer-settler flow in the column, and frequencies from approximately 65 to 200 cycles/min. caused turbulent flow. Flooding occurred below 25 and above 220 cycles/min.

Procedure

Operating temperatures were 78° to 81°F. The 0.09 weight-fraction aqueous acid solution was fed to the top of the col-

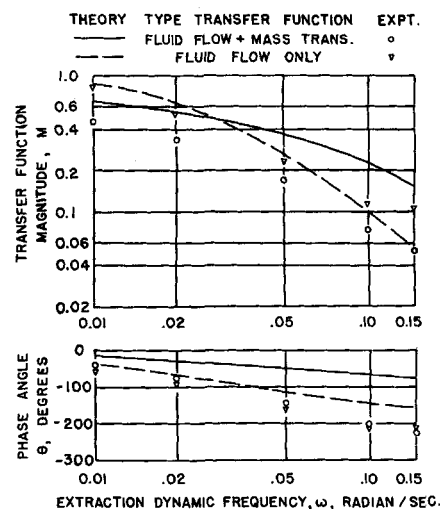


Fig. 4. Bode diagram of transfer function. Two column plates. Column pulse frequency is 30 cycles/min.

umn at a rate of 25 g/min., and the 0.035 weight-fraction solvent acid solution was fed to the bottom of the column at 30 g/min. Then column pulsation was started, and the system was allowed to come to steady state. During this time the interface at the top of the column was held 2 in. above the top plate by adjusting the raffinate throttle valve. During the last 5 min. of this period the raffinate and extract flow rates were determined experimentally by draining their flows into graduated cylinders for a specific time interval. Several samples of the raffinate and extract were also taken at specific intervals, and the acid concentration was determined to confirm the existence of steady state in the column.

After steady state had been reached, samples were taken of the raffinate and the aqueous solutions above each plate for the determination of plate efficiencies. Then an acid or dye pulse of 1-sec. duration was injected into the aqueous phase above the top plate of the column. Samples of the raffinate were taken for every 10-sec. time interval until the column returned to steady state conditions. The flow rate was again measured and the raffinate and the extract were sampled. Then the pulse-injection procedure was repeated. This procedure was followed three times for each experiment. After the last pulse, the feed and the raffinate flows were shut off simultaneously. Then the liquid in the column was drained into a graduated cylinder to determine the column holdup of the aqueous and solvent phases. Finally all the extract solution from the periods of pulse was collected and titrated to check the material balance of the pulse data.

As soon as the pulse experiment had been completed, a steady state dye experiment at the same operating conditions was made to determine the degree of backmixing in the column (6). The experiment was started in the same manner as the pulse experiment, with the addition of a continuous flow of 1 g./min. of 0.001 weight-fraction aqueous scarlet-red dye solution beneath the bottom plate. When the column reached steady state, samples of the dye in the raffinate and the aqueous solution above each plate were taken to determine the backmixing in the aqueous phase. From visual inspection of the column, the backmixing in the dispersed solvent phase was assumed negligible.

The experimental procedure was repeated for both acid and dye pulses at column pulsation frequencies of 30, 80, 150, and 210 cycles/min in the two-plate column. A pulse of 30 cycles/min. produced mixing characteristics in the middle of the mixer-settler flow region. The experiments at frequencies of 80 and 150 cycles/min. were made in the best portion of the turbulent-flow region, and the experiment at 210 cycles/min. was made in the flow region where the high turbulence was starting to flood the column. Experiments at 30 and 80 cycles/min. were also performed in a three-plate column. Steady

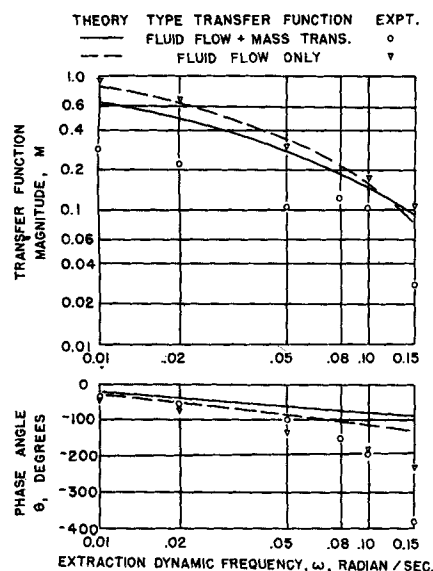


Fig. 5. Bode diagram of transfer function. Two column plates. Column pulse frequency is 80 cycles/min.

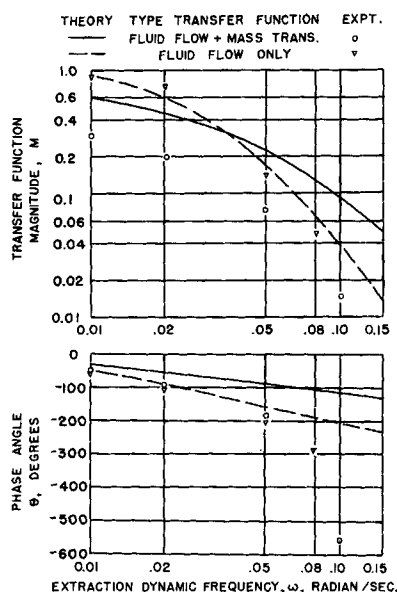


Fig. 6. Bode diagram of transfer function. Three column plates. Column pulse frequency is 30 cycles/min.

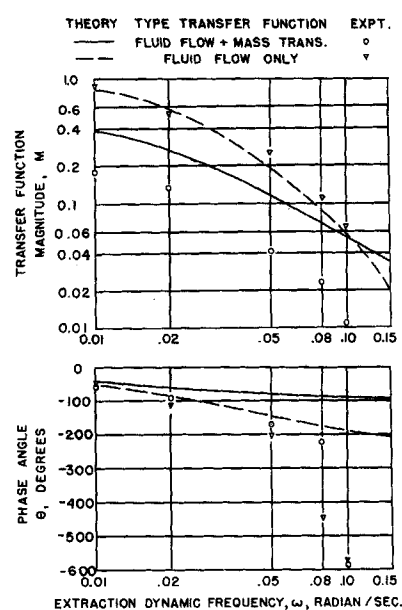


Fig. 7. Bode diagram of transfer function. Three column plates. Column pulse frequency is 80 cycles/min.

state experiments at 150 and 210 cycles/min. were made in this column to determine the corresponding values of back-mixing and plate efficiencies. The column was pulsed at increasing frequency until flooding occurred. Partial flooding of the 6-in.-high, three-plate column was noticed at the higher frequencies reported, but the 4-in. two-plate column did not flood under similar conditions.

RESULTS

Experimental results were calculated at discrete values of signal frequency on the response curve. The dynamic results are expressed in terms of the amplitude ratio magnitude, M , and the phase angle, θ , which are both functions of the signal or extraction dynamic frequency, ω . The numerical results were obtained by use of a desk calculator, and their accuracy did not justify obtaining more points than are shown. Figures 4 through 7 show Bode plots of the results with number of plates in the column and column-pulsation frequency as parameters.

The corresponding values of the stage efficiencies, eddy diffusivities, and column holdups are given in Table 1. The efficiencies are only approximate; individual stage efficiencies were based on experimental samples which may not have been truly representative. The values were substituted into Equations (11) and (13) and the corresponding equations for a three-plate column (8) to obtain the theoretical transfer functions. These expressions were manipulated algebraically to obtain relations in the form of Equations (12) and (14). The values of gain and the corresponding time constants, T_i , are shown in Table 2.

The theoretical relations are also plotted in Figures 4 through 7. In every case the experimental gain at low frequency was smaller than the theoretical gain. Comparison of experimental results and all theoretical phase-angle curves shows that the experimental phase angle increases negatively much more rapidly with increasing signal frequency, ω , than does the corresponding theoretical phase angle. Therefore, an additional dead-time expression $e^{-T_L s}$, was determined. The magnitude of its amplitude is always unity, and its phase angle is

$$\theta_{\text{dead time}} = -\omega T_L = \theta_{\text{exp}}(j\omega) - \theta_{\text{thy}}(j\omega)$$

The dead time, T_L , can be calculated at any value of ω . Thus the values of T_L shown in Table 2 are the average dead times over the experimental range of signal frequency.

Dead time was not accounted for by pure transportation lag; mixing owing to pulsation greatly decreased dead time since calculated values in Table 2 are only about one quarter of the dead times determined from transportation time alone.

CONTINUING RESEARCH

The present work was exploratory and was intentionally limited to only a few plates because a continuous method of chemical analysis was not available for studying the output. Detection of detail in the output was not thought possible. This research has been continued with the same column, a greater number of plates, a different liquid

TABLE 1. STEADY STATE EXPERIMENTAL RESULTS

Column pulse frequency, cycles/min.	Plates, no.	Eddy diffusivity, sq. cm./min.	Aqueous-phase holdup, g.	Solvent-phase holdup, g.	Efficiency			
					Overall column	Top stage	Middle stage	Bottom stage
30	2	37	29	4.0	0.69	0.43	—	0.065
80	2	99	24.5	8.8	0.82	0.66	—	0.29
150	2	127	23	8.8	0.80	0.93	—	0.19
210	2	67	25	7.6	0.69	0.54	—	0.10
30	3	24	38.5	7.2	0.69	0.35	0.11	0.46
80	3	40	36	9.6	0.90	0.60	0.28	0.29
150*	3	80	36	9.2	0.89	0.87	0.23	0.24
210*	3	123	33	12.0	0.89	0.61	0.23	0.25

* The column was partially flooded during these experiments.

TABLE 2. THEORETICAL AND EXPERIMENTAL RESULTS

Plates, no.	Column pulse frequency, cycles/min.	Theoretical					Experimental		
		Transfer function time constants, sec.					Gain, K	Gain, $\omega = 0$, K	Dead time, T_L
		Numerator		Denominator					
		T_1	T_2	T_3	T_4	T_5			
I. Combined effect of fluid flow and mass transfer									
2	30	4.08	—	3.42	29.4	—	0.65	0.56	26
2	80	4.67	—	5.84	47.1	—	0.69	0.32	19
2	150	5.11	—	4.82	36.2	—	0.49	0.38	13
2	210	6.55	—	5.06	31.6	—	0.62	0.37	17
3	30	2.26	4.36	4.10	10.4	48.0	0.64	0.36	24
3	80	3.91	3.97	4.49	5.86	75.0	0.46	0.25	26
II. Effect of fluid flow only									
2	30	—	—	17.1	55.4	—	1.00	1.00	11
2	80	—	—	6.92	55.6	—	1.00	1.00	15
2	150	—	—	5.13	60.3	—	1.00	1.00	19
2	210	—	—	8.94	52.6	—	1.00	1.00	12
3	30	—	—	17.5	26.7	49.2	1.00	1.00	15
3	80	—	—	9.89	20.3	64.4	1.00	1.00	18

system, a continuous method for chemical analysis, and computer reduction of data.

DISCUSSION OF RESULTS

The similarity of the experimental data for fluid flow alone, shown in Figures 4 through 7, indicates that the degree of turbulence in the column had little effect on the dynamics of fluid flow. However, there was a larger effect on the amplitude magnitude for the combined effect of fluid flow and mass transfer.

It was extremely difficult to determine the order of the experimental transfer functions because of the inaccuracy of the small values of the amplitude magnitude at high signal frequencies. In Equation (17) these small values are calculated from differences of large numbers. Also, the initial pulse data, which are composed mainly of the response at high frequencies, are not very accurate.

The ability of the theoretical models to predict the experimental responses depends on the degree to which the linear models describe the actual experimental behavior and on the accuracy of the experimentally determined constants (Table 2). The comparison of the experimental results with the theory shows that more sophisticated models are needed to describe the dynamic behavior accurately. More precise experimental techniques, such as continuous analysis of the system response, would also be helpful to determine the exact relation of the dynamic response as a function of the signal frequency.

NOTATION

A	= cross section of column, sq.cm.
d	= differential operator
D_L	= density of the aqueous phase, g./cc.
D_G	= density of the solvent phase, g./cc.
e_L	= eddy diffusivity in the aqueous phase, sq.cm./min.
e_G	= eddy diffusivity in the solvent phase, sq.cm./min.
E_m	= liquid plate or stage mass transfer efficiency
f	= column pulsation frequency, cycles/min.
$f(t)$	= a time-dependent function
G	= mass flow rate of the solvent, g./min.
h	= aqueous-phase stage holdup, g. of acid solution/plate
H	= solvent-phase stage holdup, g. of acid solution/plate
i	= any positive integer, 1, 2, 3, . . .
I_i	= constants defined when used

j	= square root of minus one
J	= any positive integer, 1, 2, 3, . . .
K	= gain constant
L	= mass flow rate of the aqueous phase, g./min.
$L[f(t)]$	= Laplace transform of the function $f(t)$
m	= any column stage, 1, 2, 3, . . .
M	= amplitude ratio magnitude of the transfer function
n	= number of plates in the column
r	= equilibrium coefficient, $y^* = rx$
s	= complex variables of the Laplace transform
t	= time, min. or sec.
T_i	= time constants, sec.
T_L	= dead time, sec.
x	= weight fraction of acid in the aqueous phase, g. acid/g. aqueous solution
x^*	= weight fraction of acid in equilibrium with solvent phase, g. acid/g. aqueous solution
y	= weight fraction of acid in the solvent phase, g. acid/g. solvent solution
y^*	= weight fraction of acid in equilibrium with aqueous phase, g. acid/g. solvent solution
Z	= vertical distance down the column, cm.
∂	= partial differential operator
Δ	= finite difference operator
θ	= phase angle of the transfer function, deg.
ω	= signal or extraction dynamic frequency, radians/sec.

LITERATURE CITED

1. Acrivos, Andreas, and N. R. Amundson, *Ind. Eng. Chem.*, **45**, 467 (1953).
2. Di Liddo, B. A., and R. A. Walsh, *ibid.*, **53**, 801 (1961).
3. Gray, R. L., Ph.D. dissertation, Univ. of Tennessee, Nashville, Tenn. (1961).
4. Hougen, J. O., "Proc. Seminar in Systems," p. 127, The Foundation for Instrumentation, Education and Research, New York (1958).
5. ———, and R. A. Walsh, *Chem. Eng. Progr.*, **57**, No. 3, p. 69 (1961).
6. Mar, B. W., L. D. Smoot, and A. L. Babb, *Ind. Eng. Chem.*, **51**, 1011 (1959).
7. Trautman, P. H., and J. A. Consiglio, *U.S. Atomic Energy Comm. Rept. TID-12472* (1956).
8. Watjen, J. W., D.Sc. dissertation, Univ. of Virginia, Charlottesville, Va. (1962).

Manuscript received November 5, 1962; revision received March 4, 1963; paper accepted March 11, 1963. Paper presented at A.I.Ch.E. Chicago meeting.