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Prediction of the Approach to Steady State of a Mixer-Settler Extractor*

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Summary

At present there is no reliable method of predicting the time required for a cascade of mixer-settler stages to approach steady state. Rules of thumb are used, based on the number of throughputs of the various streams. This paper compares data obtained in the laboratory for the TBP (tributyl phosphate)-Varsol-H_2O-HNO_3 system with four assumed mathematical models. It was found that the model that assumed homogeneity of the aqueous phase in the settling chamber and plug flow of the organic phase in the settling chamber predicted the nitric acid concentrations most accurately. In the absence of other information, this model is recommended for prediction of results for tube-type mixer-settler extractors for systems with similar properties.

It was of considerable interest that simpler models could be used for accurate estimates when the number of stages in the cascade was increased.

Mixer-settler extractors have been used rather extensively in the past two decades. Multistage extractors made from glass tubes have been used in the laboratory to study separations on a small scale, and box-type units have been used frequently for continuous larger-scale separations. At the present time there is no reliable method of estimating the time required for a mixer-settler to approach steady state, and few previous studies have been devoted to the effect of flow characteristics within the extractor on the response of the system.

This paper describes how well various mathematical models developed for the extraction system were able to predict the con-

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[*] Contribution No. 1798. Work was performed at the Ames Laboratory of the U.S. Atomic Energy Commission.

centration of nitric acid in the effluent streams in a continuous countercurrent tube-type mixer-settler cascade as a function of time using tributyl phosphate plus Varsol[*] as one solvent and water as the other. The response of the system was obtained as a function of time after a step change in feed concentration had been made.

Staffin and Chu (2) considered the unsteady-state characteristics of continuous extraction in an agitated vessel to determine if a relationship could be found between the transfer functions derived from the response curve observed after a step change in concentration in one of the input streams and the mechanical and physical properties of the system. They were unable to correlate their results in terms of the transfer functions obtained from the observed experimental data and concluded that better analytical techniques were needed to obtain the necessary data.

The work of Farris and Burkhart (*1*) in developing DIAN, a system for programming a digital computer in terms of analog components, was particularly applicable to this problem. This system retains much of the simplicity of programming in the analog sense, but has many of the advantages of digital computations.

DESCRIPTION OF DIAN COMPONENTS

A brief description of the operations performed by the DIAN components used in this study is given below. A more detailed discussion can be found in the paper by Farris and Burkhart (*1*).

The integrators, shown schematically in Fig. 1, are somewhat different from analog-computer integrators in that they use two types of inputs, primary and secondary. The primary input to an integrator may be the differential of any function of the independent or dependent variables. This makes possible the generation of many nonlinear functions using combinations of the basic components.

Empirical-function generators permit functional relationships to be defined empirically in terms of discrete datum points. In our work this component was used to generate the equilibrium relationship.

The summer and constant multiplier are analogous in operation to their analog-computer counterparts, except that the multiplicative constant is not restricted to values less than 1.

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[*] Varsol is a purified fraction of C_9 and C_{10} hydrocarbons sold by Humble Oil and Refining Company.

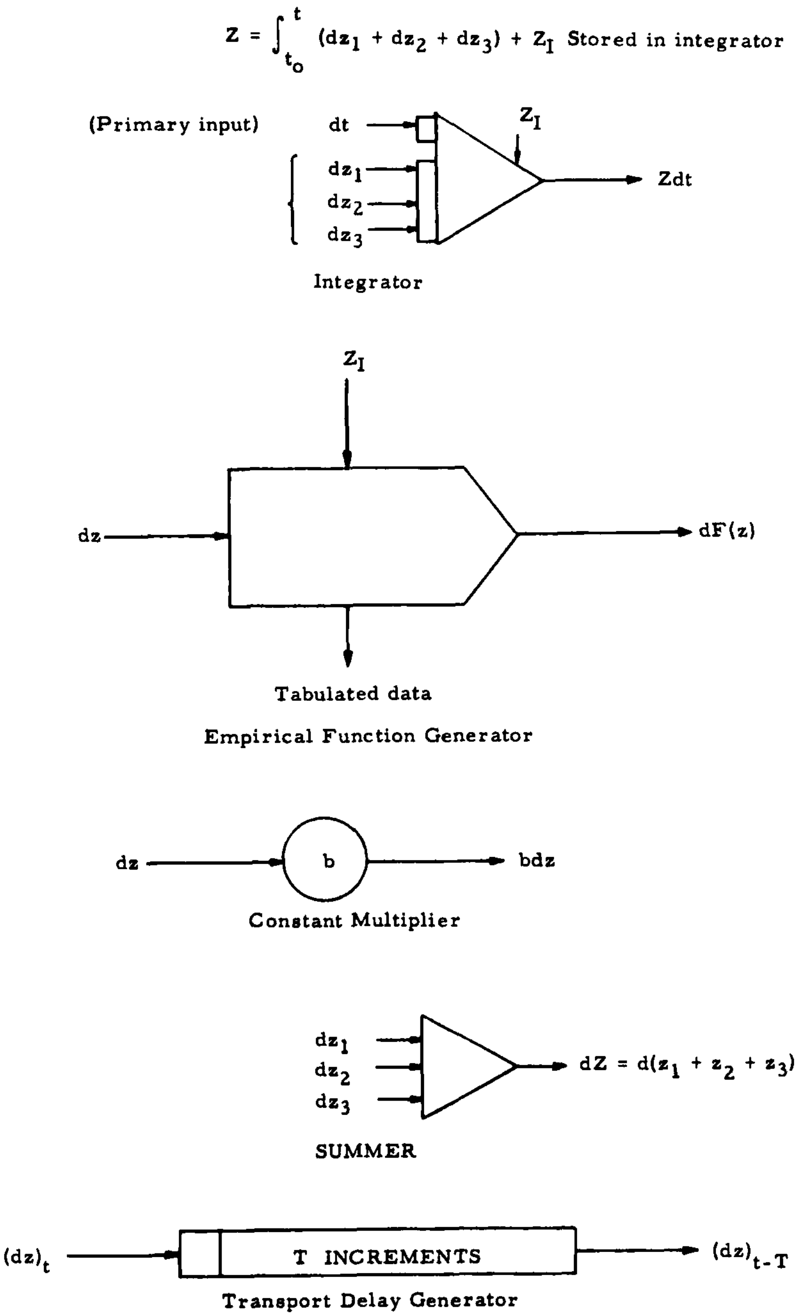


FIG. 1. Schematic representation of the operations performed by the DIAN components.

Transport-delay generators allow an exact representation of time lag due to material transport. They were used to simulate the response of material in plug flow.

MIXER-SETTLER MODELS

In a mixer-settler extractor the entering streams to a stage are mixed intimately in a mixing chamber and flow concurrently to a settling chamber through a transfer line. In many designs this transfer line is eliminated, and only an overflow weir separates the mixing and settling chambers. In this study it was assumed that no mass transfer took place in these transfer lines. After entering the settler, the two streams disengage and flow countercurrently to the preceding and succeeding stages in the cascade.

Analog relationships were assumed for each part of an individual stage, and the responses from each were combined to simulate the changes taking place in a given stage as a function of time. The responses from the individual stages were then combined to simulate the behavior of a multistage extractor.

MIXING CHAMBER

In all the models the fluids in each of the mixing chambers were assumed to be perfectly mixed with the aqueous and organic phases in equilibrium. However, a stage efficiency that was either constant or a function of concentration could have been easily incorporated in the models.

The equilibrium relationship was assumed to be a monotone-increasing function that could be adequately represented by a reasonable number of datum points using parabolic or linear interpolation. The fact that the equilibrium relationship can be expressed in terms of an array of datum points is one of the significant advantages of DIAN.

Equation (1) is the unsteady-state mass balance for the ith-stage mixing chamber shown in Fig. 2, assuming perfect mixing, constant flow rates, constant volumes, and 100% stage efficiency.

$$dX_M = \frac{HX_{i-1}\,dt}{v_H} + \frac{LY_{i+1}\,dt}{v_H} - \frac{HX_M\,dt}{v_H} - \frac{LY_M\,dt}{v_H} - \frac{v_L\,dY_M}{v_H} \qquad (1)$$

This equation was programmed using DIAN to obtain the response

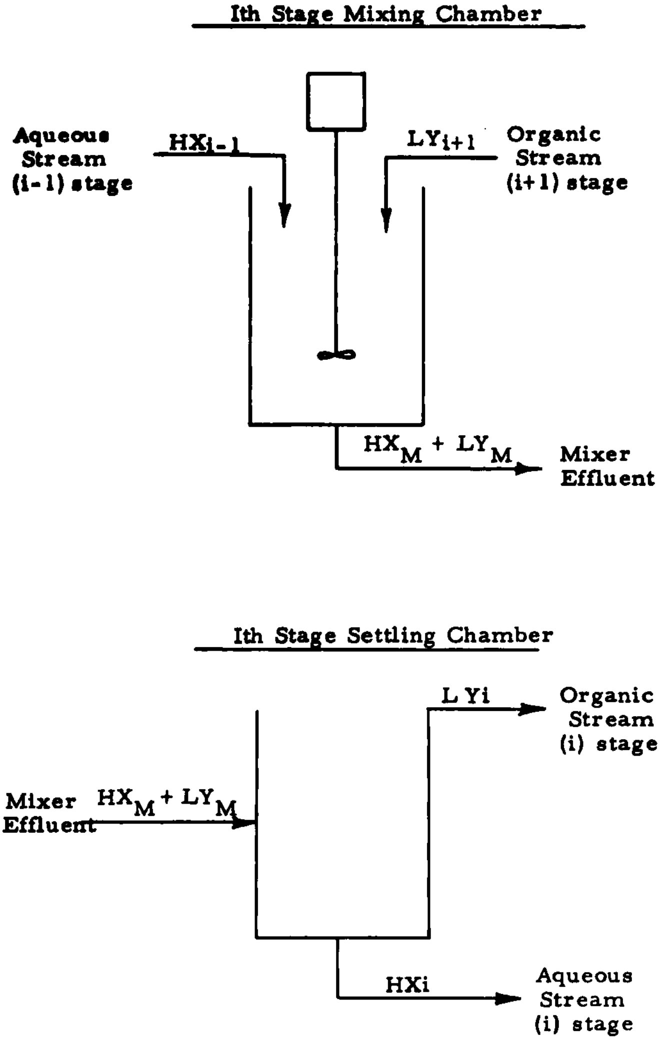
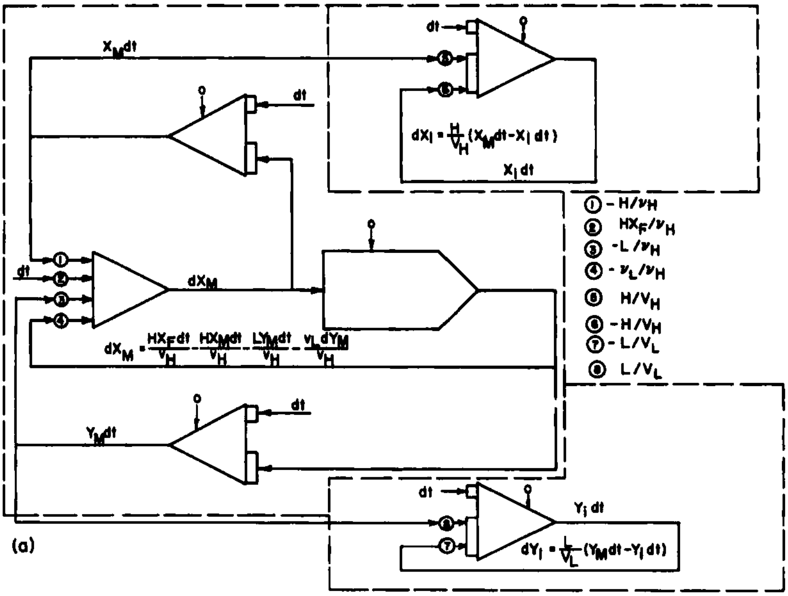


FIG. 2. Flow diagram for the *i*th stage in the extractor.

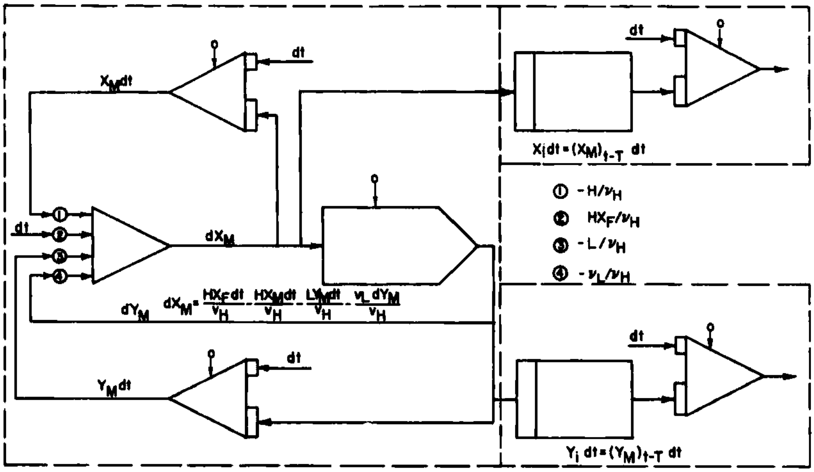
of the fluid in the mixing chamber to a step change in nitric acid concentration in the incoming aqueous stream.

SETTLING CHAMBER

The streams leaving the mixer were assumed to disengage immediately upon entering the settler with no further mass transfer. The


$X_M dt$
dt
0
$dX_I = \frac{H}{V_H}(X_M dt - X_I dt)$
$X_I dt$
① $-H/\nu_H$
② HX_F/ν_H
③ $-L/\nu_H$
④ $-\nu_L/\nu_H$
⑤ H/V_H
⑥ $-H/V_H$
⑦ $-L/V_L$
⑧ L/V_L
dX_M
$dX_M = \frac{HX_F dt}{\nu_H} - \frac{HX_M dt}{\nu_H} - \frac{LY_M dt}{\nu_H} - \frac{\nu_L dY_M}{\nu_H}$
$Y_M dt$
$Y_I dt$
$dY_I = \frac{L}{V_L}(Y_M dt - Y_I dt)$

(a)


$X_M dt$
dt
0
$X_I dt = (X_M)_{t-T}\, dt$
① $-H/\nu_H$
② HX_F/ν_H
③ $-L/\nu_H$
④ $-\nu_L/\nu_H$
dX_M
dY_M
$dX_M = \frac{HX_F dt}{\nu_H} - \frac{HX_M dt}{\nu_H} - \frac{LY_M dt}{\nu_H} - \frac{\nu_L dY_M}{\nu_H}$
$Y_M dt$
$Y_I dt = (Y_M)_{t-T}\, dt$

(b)

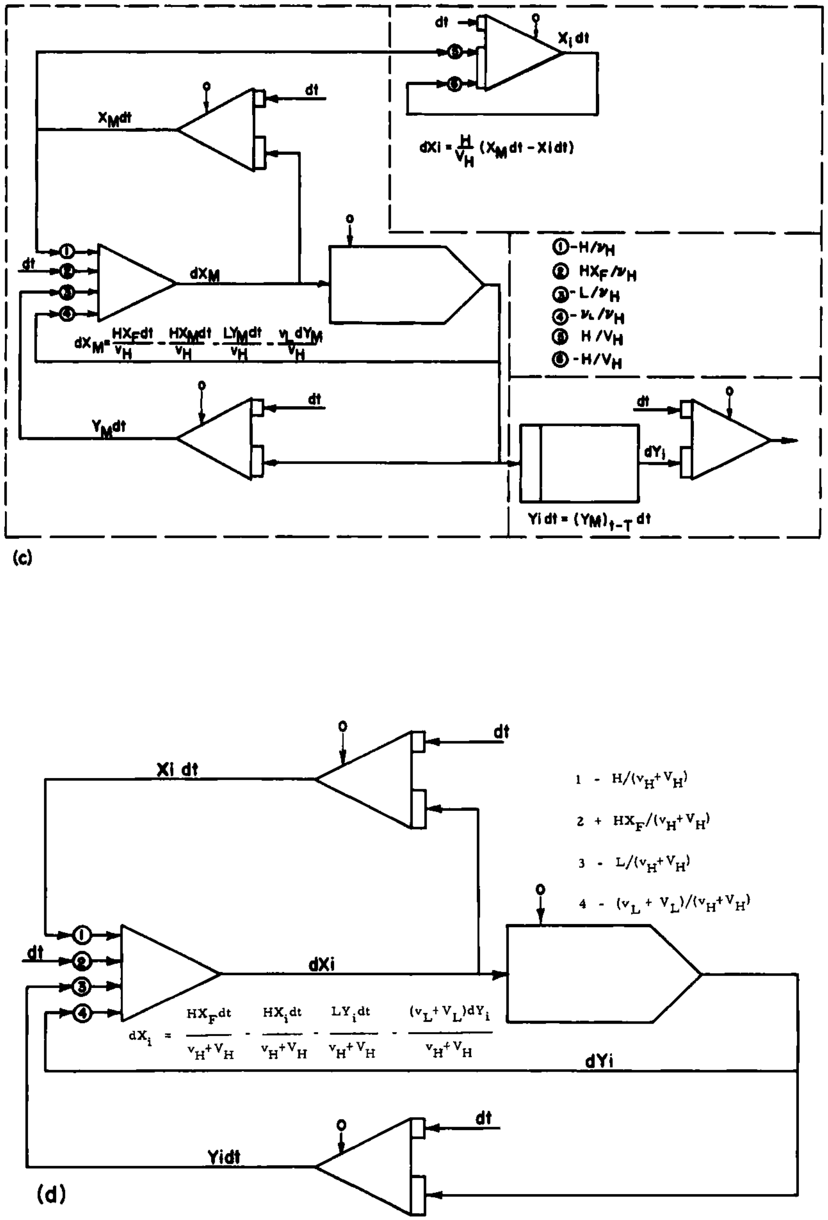


FIG. 3. DIAN diagrams for the single-stage models. (a) Perfectly mixed model; (b) plug flow model; (c) hybrid model; (d) equilibrium model.

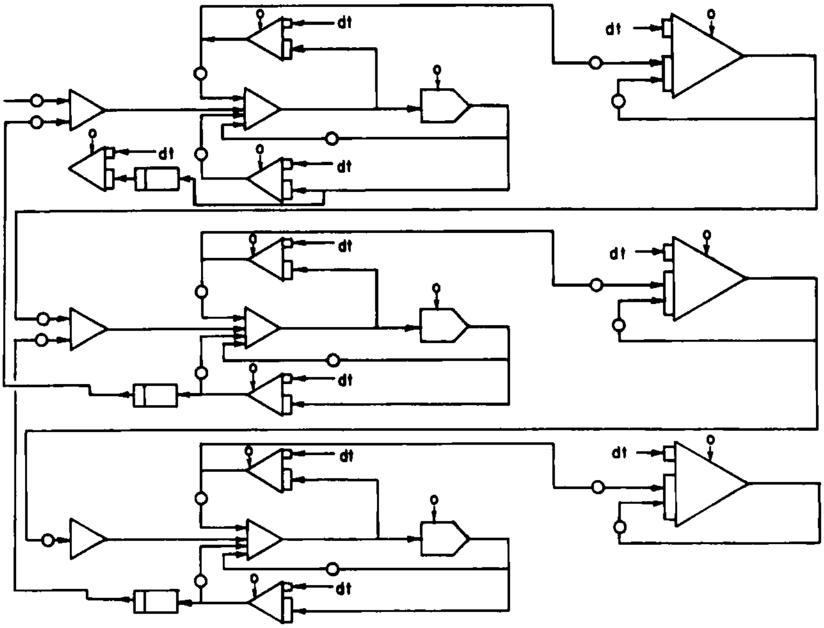


FIG. 4. DIAN diagram for a three-stage extractor—hybrid model.

volume in the settler through which either of the phases had to flow before leaving was assumed to be constant and equal to the volume of that phase in the settler.

Additional assumptions were necessary concerning the type of flow of the phases in the settling chambers. In one case it was assumed that each phase was of constant composition and that the inlet and exit flow rates were equal. If this assumption, together with the assumptions of constant flow rates and constant volumes, are satisfied, the response of each of the phases can be obtained from an unsteady-state mass balance. Equation (2) is such a balance for the aqueous phase in the settler (Fig. 2).

$$dX_i = \frac{H}{V_H} (X_M\, dt - X_i\, dt) \tag{2}$$

When this type of mass balance was applied to both phases in the settling chambers, the model was called the *perfectly mixed model.*

If both phases in the settler were assumed to be in plug flow, the model for the mixer-settler unit was referred to as the *plug-flow model.* When the organic phase was assumed to flow through the settling chambers in plug flow and the aqueous phase was assumed to be homogeneous in the settling chamber, the model was called the *hybrid model.* A fourth model was called the *equilibrium model.* This model assumes that the mixer and settler of each stage form a single vessel, that both phases are homogeneous at all times, and that the stage is ideal.

Diagrams showing how all four models were programmed to simulate the response of a single-stage extractor when the nitric acid concentration of the organic feed was assumed to be zero are shown in Fig. 3. Figure 4 shows how the single-stage units were combined to simulate the response of a three-stage extractor for the particular case of the hybrid model. The other models were combined in a similar manner.

EXPERIMENTAL PROCEDURE

The experimental equipment consisted of the extractor and the necessary tubing, tanks, pumps, and flow meters. The aqueous phases flowed from their respective head tanks through rotameters to three-way valves located at a junction point just in front of the entrance to the extractor. A rotameter was also used to measure the flow rate of the organic stream which entered the extractor at the top of the mixing chamber. The fluid in the mixing chamber was agitated using a flat Plexiglas paddle blade powered by a variable-speed drive. The mixer effluent entered a port midway up the settler, and, after disengaging, the two phases left via their respective outlet ports. The mixer and settler were both Plexiglas cylinders whose inside diameter was 4 inches and height 17 inches.

In the three-stage extractor, the flow of the aqueous phase was due to differences in head. Interstage pumps were used to move the organic phase. A schematic flow diagram of the system is given in Fig. 5.

Prior to a run the extractor was drained and the system flushed with distilled water. The mixer and settler were then filled with both phases to approximately the desired levels. The mixer was started and the flow rates adjusted. The system was allowed to come to hydraulic equilibrium, and the volumes of the phases in the settler were adjusted to any desired values.

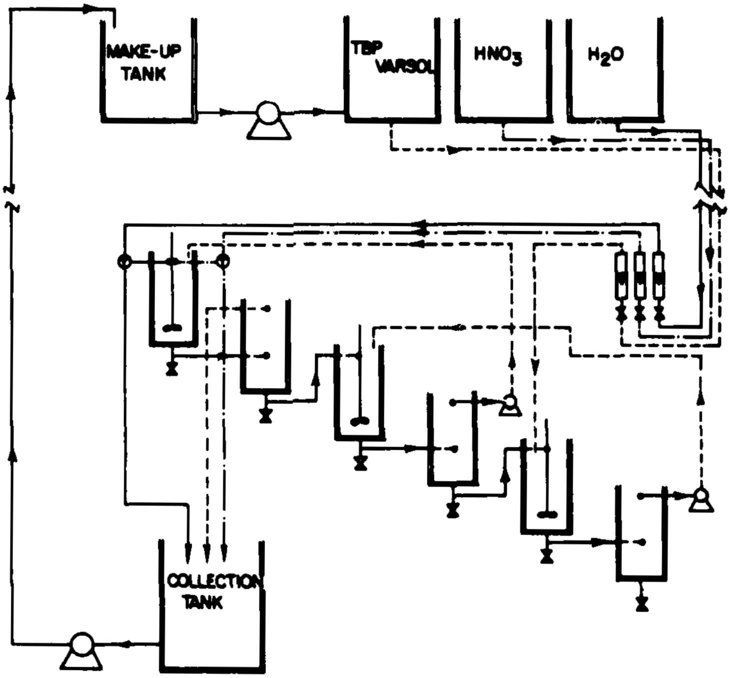


FIG. 5. Flow diagram for the three-stage extractor.

At the beginning of a run, the acid stream was directed toward and the water stream directed away from the extractor by rotating two three-way valves. Simultaneously the timer was started and any necessary rotameter corrections made. Samples were then taken from the extractor effluent streams or from snap valves located below the tees on the bottom of the vessels.

The run was continued with samples being taken periodically as the system approached steady state. A condition of near steady state was determined either by previous experience or by spot checking the effluent concentration.

After stopping all flows, the volume of each of the phases in each of the chambers was determined. This volume was then converted to pounds of acid-free phase, because this is less subject to change as the concentrations change. The weight of the organic acid-free phase in the settler was varied from 1.4 to 3.6 lb over the series of runs. The weight of the acid-free aqueous phase was varied from 1.9 to 4.5 lb. These conditions resulted in the settler operating at its maximum and minimum organic content consistent with stable operating conditions.

The flow rates were also expressed on an acid-free weight basis. These rates were varied from 16 to 54 lb/hr for the organic phase and 21 to 55 lb/hr for the aqueous phase over the series of runs. The feed concentration ranged from 0.125 to 0.155 lb of acid per pound of acid-free water.

DISCUSSION OF RESULTS

Error Evaluation

Although it was possible to determine by inspection of concentration versus time plots which model best simulated the observed response of the extractor for many of the runs, a quantitative measure of the "degree of fit" was desired. The integral average per cent error shown in Eq. (3) was defined for this purpose.

$$E_{(C_1-C_2)\%} = \frac{100 \int_{t_1}^{t_2} |C_e - C_p|/C_e \, dt}{t_2 - t_1} \tag{3}$$

The integration limits, t_1 and t_2, correspond to the concentrations C_1 and C_2. These concentrations are expressed as a per cent of the steady-state value and are obtained from the concentration versus time plot of the experimental data. The concentrations C_p and C_e are, respectively, the concentrations predicted by the model being considered and the experimentally observed concentration of nitric acid, both expressed as pounds of acid per pound of acid-free phase.

Each of the four mathematical models was based on the assumption that the system is subject to a true step change. Because it was not actually possible to effect such a change, the error indicated by Eq. (3) would not be a good test of the models at the very beginning of a run. Furthermore, the calculated error is highly dependent upon an accurate measurement for C_e, the experimental concentration of nitric acid. The technique used in this investigation would not give reliable values for C_e for very low concentrations. For these reasons, no acid concentrations below 3% of the steady-state concentration were used in determining the "degree of fit" of the models.

At the end of the run the concentrations in the effluent streams became asymptotic to the steady-state values. Because of the slow approach to steady state many of the runs were terminated when the concentration in the effluent streams closely approached the steady-state values. Ninety per cent of steady state was therefore arbitrarily chosen as the upper limit. The error evaluated over this interval would then be $E_{(3-90)\%}$.

Two other time intervals were arbitrarily chosen to compare the "degree of fit" at the beginning of a run and after the initial change was accomplished. The error at the beginning of the run was measured using $E_{(3-10)\%}$ and the error after the initial change using $E_{(10-90)\%}$.

PERFORMANCE OF MIXERS

The assumption of perfect mixing in the mixing chamber with the effluent streams in equilibrium with each other was found to be reasonable under normal operating conditions. This assumption was tested by comparing the predicted and observed nitric acid concentrations in the aqueous stream leaving the mixer. Figure 6 is a representative example of the close agreement between the predicted and observed concentrations in the mixer effluent. This close agreement between the experimental and predicted concen-

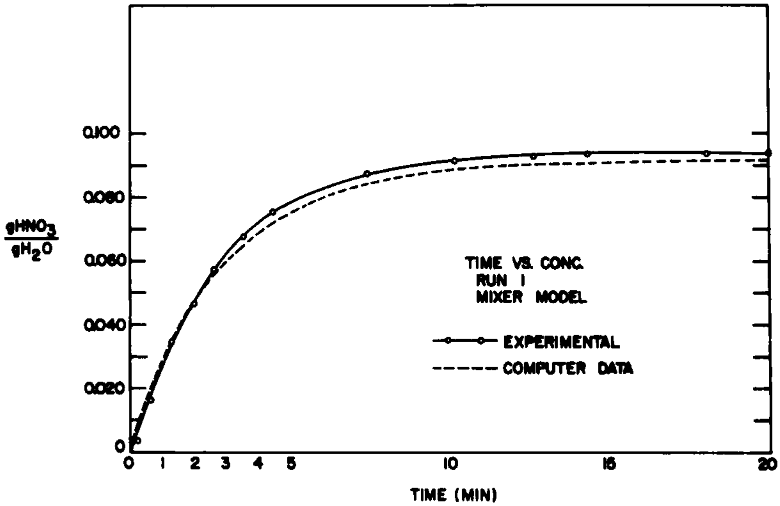


FIG. 6. Comparison of the predicted and observed concentrations in the mixer effluent during a typical run.

trations of nitric acid in the effluent stream from the mixing chamber indicated that errors in the simulation of stage behavior were due to errors in simulating the response of the settlers.

PERFORMANCE OF SETTLERS

Single-Stage Runs

An examination of the error data indicated that the observed concentrations in the organic stream leaving the settler were consistently predicted best by the plug-flow model over all the concentration intervals considered. The average of the values of $E_{(3-90)\%}$ measured for the organic phase leaving the settler in the single-stage runs was 34% for the plug-flow model, 84% for the perfectly mixed model, and 128% for the equilibrium model.

The perfectly mixed model consistently provided the best prediction of the observed nitric acid concentrations in the aqueous stream leaving the settler over all the concentration intervals considered. The average of the values of $E_{(3-90)\%}$ measured for this stream were 15%, 34%, and 55% for the perfectly mixed model, plug-flow model, and equilibrium model, respectively.

In the single-stage unit there is no feedback from the settler to

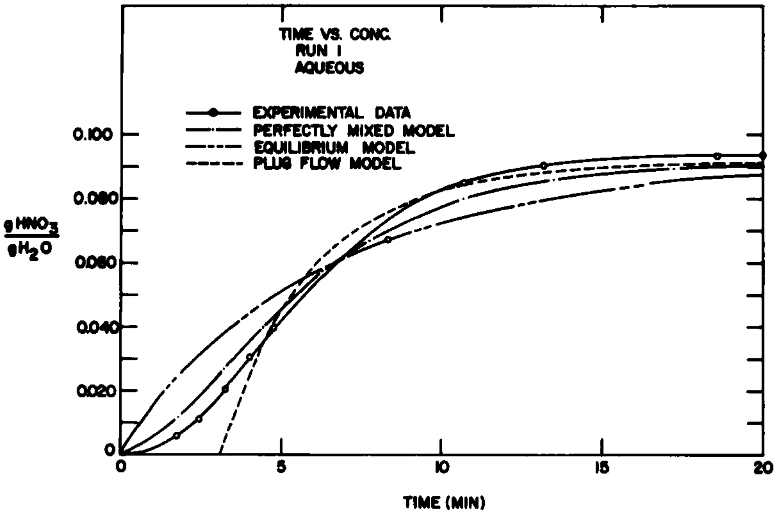


FIG. 7. Nitric acid concentration of the aqueous phase leaving the settler versus time for the single-stage run 1.

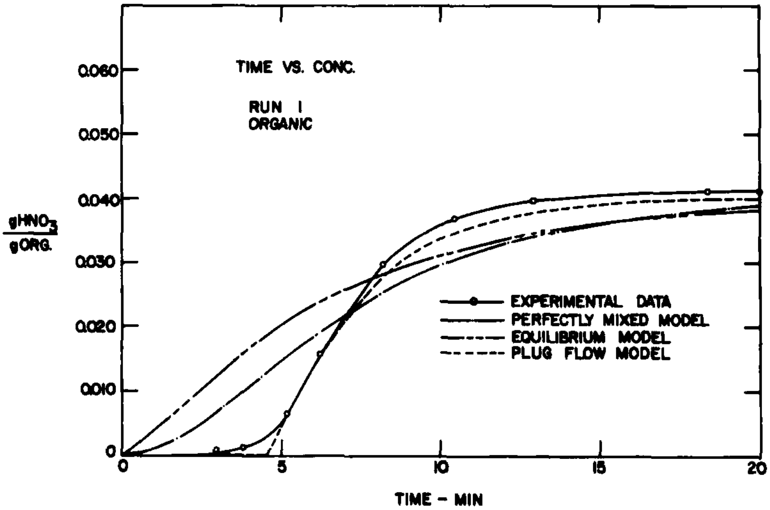


FIG. 8. Nitric acid concentration of the organic phase leaving the settler *versus time for the single-stage run* 1.

the mixer, so the response of the hybrid model can be obtained by combining the response of the organic phase as predicted by the plug-flow model and the response of the aqueous phase as predicted by the perfectly mixed model. The hybrid model, therefore, best predicts the experimental nitric acid concentrations in both of the leaving streams for all the single-stage runs over all the concentration intervals for which the error was measured. A typical set of predicted and observed response curves is shown in Figs. 7 and 8.

Three-Stage Runs

The plot of the nitric acid concentrations showed that the response curves predicted by each of the models were very similar when a three-stage extractor was considered. This can be seen in Fig. 9, which shows the observed as well as the predicted concentrations in the effluent organic stream for a three-stage run. For this run, the responses predicted in the organic stream by the hybrid model, plug-flow model, and perfectly mixed model were practically coincident in all but the initial portion of the run.

The average error, $E_{(3-90)\%}$, was measured for the concentrations in the effluent streams leaving the three-stage extractor. For both

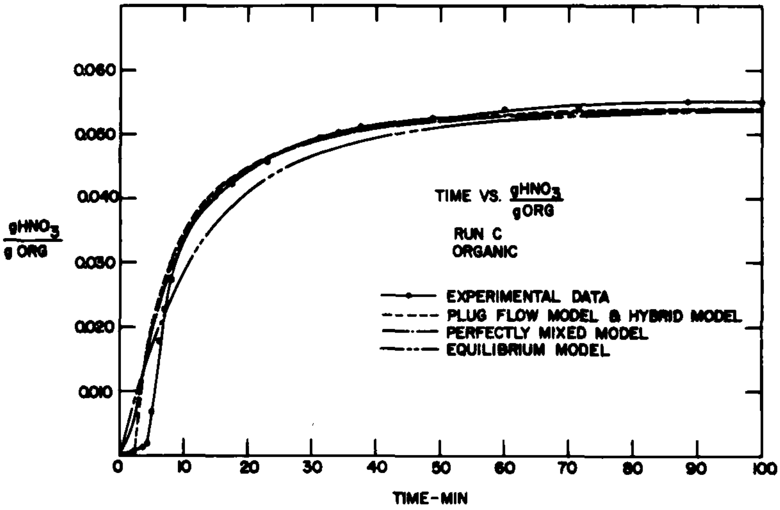


FIG. 9. Comparison of the concentrations predicted by the various models and that observed in the organic phase leaving the settler—three-stage run.

these streams the average error of the concentrations predicted by each of the models decreased 10% or more from the averages reported for the single-stage runs. In particular, the average value of $E_{(3-90)\%}$ for the hybrid model was only 23% for the effluent organic stream and 3% for the leaving aqueous stream.

The hybrid model that combines the best features of the perfectly mixed model and the plug-flow model was slightly superior to the other three models, but the results predicted by all three were of nearly the same accuracy. However, this model would still be recommended when simulating a three-stage extractor if no other criteria were available.

Six-Stage Run

It was observed that the responses predicted by each of the models were more similar for the three-stage extractor than they were for the single-stage unit. To see if this trend continued, a six-stage extractor was simulated on the computer using the volumes and flow rates measured in a three-stage run. A plot of the concentrations predicted by each of the models indicated that the responses were almost coincident (Figs. 10 and 11).

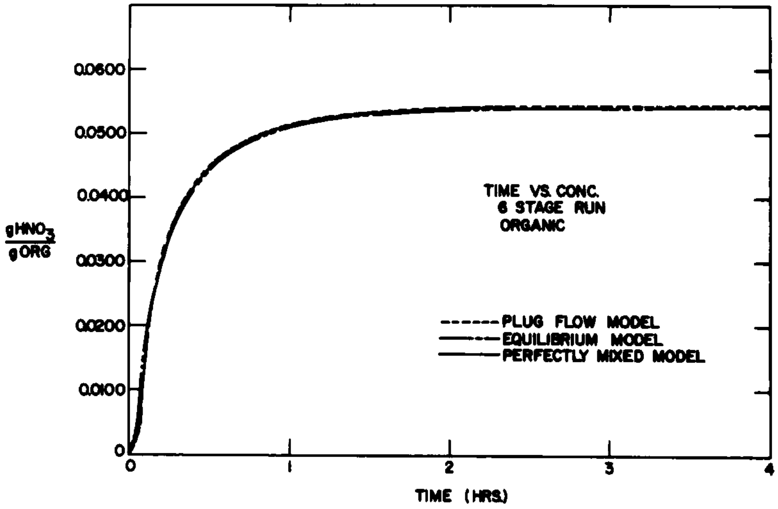


FIG. 10. Comparison of the concentrations predicted in the exit organic phase from a six-stage extractor.

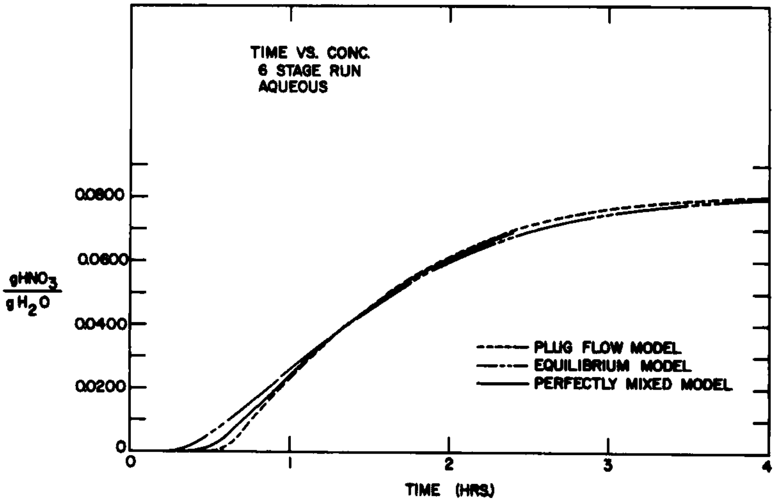


FIG. 11. Comparison of the concentrations predicted in the exit aqueous phase from a six-stage extractor.

CONCLUSIONS

All four models predicted similar curves for the nitric acid concentrations as a function of time when applied to multistage systems. These curves tended to converge to a common curve as the number of stages in the cascade became larger.

The hybrid model provided the best prediction of the extractor output concentrations in almost all the different situations of flow and stage volumes considered. This model was consistently the best for the single-stage runs, and was the equal of the others in the three-stage case. In the absence of other information, its use is recommended for prediction of results for tube-type mixer-settler extractors for systems in which the properties of the phases are similar to that of water and a 50% tributyl phosphate–50% Varsol mixture.

The reason the hybrid model gave the best reproduction of experimental data is not known, but it may be due to the flow characteristics in the disengaging section of the settling chamber. In this section, the aqueous phase appeared to be the continuous phase and the organic phase passed through this region as discrete droplets. These droplets would tend to respond as material in plug flow, and their movement would cause mixing of the aqueous phase.

Nomenclature

A	aqueous phase
C	nitric acid concentrations lb nitric acid/lb acid-free phase
E	integral average per cent error
H	aqueous-phase flow rate, lb acid-free phase/hr
L	organic-phase flow rate, lb acid-free phase/hr
O	organic phase
T	time delay, hr
t	time, hr
V	pounds of acid-free phase in settling chamber
v	pounds of acid-free phase in mixing chamber
X	aqueous-phase nitric acid concentration lb nitric acid/lb acid-free phase
Z	dummy variable
z	dummy variable

Subscripts

e	experimental
F	feed
H	aqueous phase
i	arbitrary stage number
I	initial value
M	mixing chamber
P	predicted
L	organic phase

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