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Extractive Reaction: Batch- and Continuous-Flow Chemical-Reaction Systems, Concentrated Case

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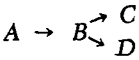
The theory of extractive reaction is extended to concentrated solutions where the distribution coefficients are no longer constant and where important changes in phase volumes may occur. The methods developed are applicable to simple or complex reactions of any order. Two- and one-solvent systems are treated, and convenient graphical methods are developed and illustrated with numerical examples.

The yield of many reversible and irreversible reactions can be increased by the deliberate, controlled addition to the reaction system of an immiscible, extractive solvent phase (*8*). Such processes, which we have labeled *extractive reactions*, encompass several unit operations. They have often been used in industrial and laboratory practice without the common character of these apparently different operations being recognized. For example, for many years simultaneous reaction and distillation have been used to shift the equilibrium of such reactions as esterification and ester exchange (*1, 2, 6*). It will be seen here that the yield of other types of reactions, for example



$A \rightarrow B \begin{smallmatrix} \nearrow C \\ \searrow D \end{smallmatrix}$, can likewise be increased over single-phase processes. Gas-absorption operations with simultaneous chemical reaction have been and continue to be the subject of numerous publications (9). Hofmann (*5*), for example, has recently shown how the conversion of pentosane to furfural can be increased by adding a solvent to the reacting system.

In a preceding paper two-solvent, two-phase extractive reactions occurring in batch or continuous stirred-tank reactor (CSTR) systems were considered, and complete analytical solutions were obtained for cases where the concentrations of the reactants are so low that the ratio of the two phases and the partition coefficients is constant (*8*).

The more complex problems of high concentrations and of reactions of any order are examined here. The limiting case of one-solvent systems is also considered, and convenient graphical solutions based on ternary equilibrium diagrams are developed.

Homogeneity within each phase and physical equilibrium between the two phases are, as before, assumed to result from sufficient agitation. Thus rates of mass transfer are herein considered not to affect the over-all rates of the reaction processes. Reaction is considered to occur in only one phase, no reaction occurs at the interface, and isothermal conditions prevail (*8*).

CONCENTRATED TWO-SOLVENT, TWO-PHASE SYSTEMS

Batch Systems

Consider a two-solvent, two-phase extractive-reaction batch process in

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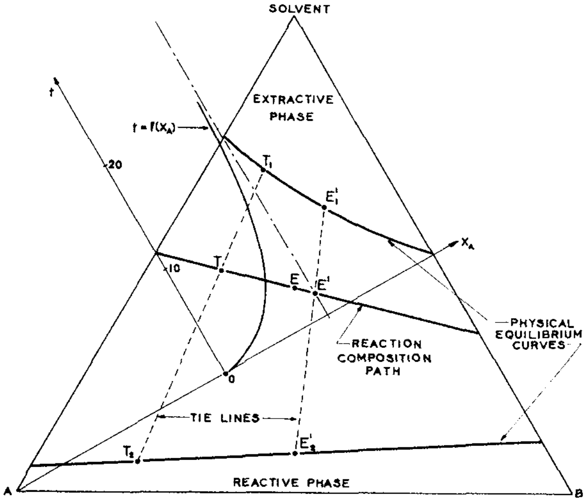

Fig. 1. One-solvent, two-phase extractive reaction. Batch process $A \rightleftharpoons 1\ B$.

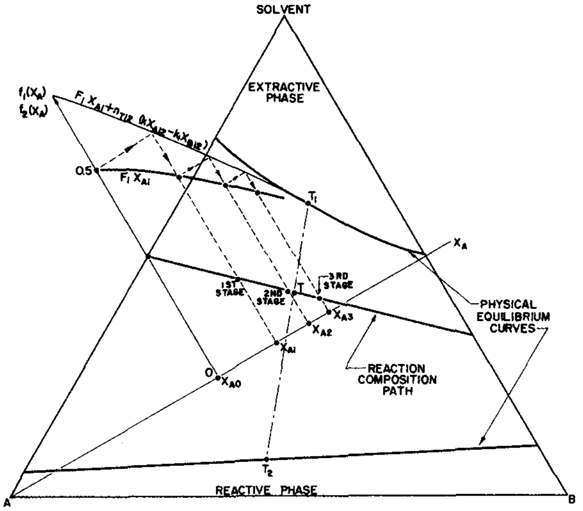

Fig. 2. One-solvent, two-phase extractive reaction, concurrent CSTR arrangement $A \rightleftarrows 2B$.

which M components are taking part in the reactions. For the elementary case of low concentration of reactants and products the mole ratio $x_1, x_2 \dots x_M$ of each component is obtained by solving the following set of differential equations:

$$\frac{dx_1}{dt} = f_1(x_1, x_2 \dots x_m) \qquad (1a)$$

$$\frac{dx_2}{dt} = f_2(x_1, x_2 \dots x_m) \qquad (1b)$$

$$\cdot$$

$$\cdot$$

$$\frac{dx_M}{dt} = f_M(x_1, x_2 \dots x_m) \qquad (1M)$$

The number of independent variables is equal to the number of components playing a role in the kinetics minus the number of independent stoichiometric relations existing between these same components; that is $m = M' - S'$ (8). For first- or zero-order reactions $f_1, f_2 \dots f_M$ are linear functions of $x_1, x_2 \dots x_m$, the coefficients of which are combinations of the reaction-rate constants, the phase ratio, and the partition coefficients. When the last quantities are constant, the general methods of solution for sets of first-order, linear differential equations are applicable.

If the reactions are not of first- or zero-order, or if the partition coefficients or reaction-rate constants depend on concentration, the above differential equations are nonlinear. Especially at high reactant concentrations, R is usually not constant but depends upon the concentrations of the M components present: that is $R = R(x_1 \dots x_M)$, with the result that the f_j's are nonlinear functions of m variables. In this case $m = M - S$.

Continuous Stirred-Tank Reactor Systems

Concurrent arrangement. A concurrent CSTR extractive reaction system in which M components are taking part in the reactions will be considered. If the concentrations of reactants and products are low enough and if the reactions are zero or first order, the molal balances around the i^{th} stage, as shown previously, lead to a set of difference equations (8):

$$F_{(i-1)}x_{1(i-1)} = f_1(x_{1i}, x_{2i}, \dots x_{mi}) \quad (2a)$$

$$F_{(i-1)}x_{2(i-1)} = f_2(x_{1i}, x_{2i}, \dots x_{mi}) \quad (2b)$$

$$\cdot$$

$$\cdot$$

$$F_{(i-1)}x_{M(i-1)} = f_M(x_{1i}, x_{2i}, \dots x_{mi}) \quad (2M)$$

where $f_1, f_2, \dots f_M$ are linear functions of the m independent variables $x_{1i}, x_{2i}, \dots x_{mi}$, with the coefficients being combinations of reaction-rate constants, flow rate, phase ratio, and partition coefficients. In this case an analytical solution can be arrived at, the number of difference equations to be solved simultaneously being $m = M' - S'$.

If the reactions are not of zero or first order, or if the partition coefficients or reaction-velocity constants depend on the concentration of the components; that is $\alpha_j = \alpha_j(x_j)$, the difference equations (2) are no longer linear, an analytical solution cannot generally be found, and stage-by-stage numerical procedures are usually employed (3).

When the concentrations of the reactants are so high that R_i and F_i depend upon the concentrations of every component M, that is $R_i = R(x_{1i}, x_{2i}, \dots x_{Mi})$ and $F_i = F(x_{1i}, x_{2i}, \dots x_{Mi})$, then the f_j's become nonlinear functions of m variables, with $m = M - S$.

If the total number of moles does not change during the reaction, then since F is a molal flow rate, $F_{(i-1)} = F_i = F$ even when changes in phase volumes occur along a chain of reactors. Variations in the factor ϵ, where $\epsilon = (F_{i1}/F_{i2})(1/R_i)$, may need to be taken into account.

When recirculation of the reactive phase is used, and if a stage-by-stage solution is needed, the effect of the recycle stream can be evaluated only by a trial-and-error procedure, because the feed composition is known only when the separator outlet stream has been calculated.

Crosscurrent arrangement. Since a crosscurrent arrangement is not conservative, the stoichiometric relations are not applicable for analytical solutions of a series of reactors (8). The number of variables will be $m = M'$ in the dilute case and $m = M$ in the concentrated case. When a stage-by-stage solution is required, then, as in the concurrent arrangement, $m = M' - S'$ or $m = M - S$ depending upon whether or not phase-volume variations occur along the chain. Of course a single crosscurrent stage is identical to a concurrent one.

Countercurrent arrangement. The conclusions regarding the value of m for the crosscurrent arrangement are applicable to the countercurrent case. The solution will in general be stage-by-stage. The difference equations of the set describing the system are of second order, and hence two consecutive values of the variables are needed for the solution, for example $x_{1o2}, x_{2o2} \dots x_{Mo2}$ and $x_{112}, x_{212} \dots x_{M12}$. However usually only the inlet stream compositions are known, that is $x_{1o2}, x_{2o2} \dots x_{Mo2}$ and $x_{1(N+1)1}, x_{2(N+1)1} \dots x_{M(N+1)1}$. When one assumes values of $x_{112}, x_{212} \dots x_{M12}$, the corresponding value of $x_{1(N+1)1}$ can be calculated and the procedure repeated until calculated and actual values for the inlet stream of solvent are in agreement. Such trial-and-error procedures are generally required for the solution of boundary-value problems of this type (*4*).

ONE-SOLVENT, TWO-PHASE SYSTEMS

In the preceding section two-solvent, two-phase systems were considered wherein each solvent was the major part of either the extractive or the reactive phase. However if the concentrations of the reactants are increased, a limiting case is reached where only one solvent, that is an extractive-phase solvent, is used. The major part of the reactive phase in this case consists of reactants and products. For example the reaction of acetic acid with glycerol can be carried out in a two-solvent system by mixing acetic acid, glycerol, toluene, and water. If only acetic acid, glycerol, and toluene are used, a one-solvent system will result.

Since convenient representations of mutual solubility data are limited to three components, the following will be concerned only with systems formed by one solvent and two reactants. A first-order reversible reaction of stoichiometry $aA = bB$ will be used to show how graphical solutions can be applied to batch or CSTR extractive-reaction processes. The graphical methods of solution developed here are applicable to reactions of any order. The rate constants may or may not depend on concentration. However for simplicity of computation first-order reactions, with reaction-velocity constants independent of concentrations, will be used in the examples.

Since the reaction $aA \rightleftharpoons bB$ is stoichiometrically simple, the reaction composition path will be the same whatever type of process is used, that is batch or tubular or a CSTR arrangement (*10*). This path is a consequence of the stoichiometric relations,

$$x_A + x_B + x_S = 1 \qquad (3)$$

$$x_B = \frac{n_B}{n_T} = \frac{\frac{b}{a}(n_{A_o} - n_A) + n_{B_o}}{n_{S_o} + n_A + n_{B_o} + \frac{b}{a}(n_{A_o} - n_A)} \qquad (4)$$

$$x_A = \frac{n_A}{n_T} = \frac{n_A}{n_{S_o} + n_A + n_{B_o} + \frac{b}{a}(n_{A_o} - n_A)} \qquad (5)$$

By introducing various values of n_A into the above relations, x_S, x_A, and x_B can be calculated from initial conditions and the reaction composition paths, that is the mixed effluent composition curve, constructed as shown in Figures 1 and 2. If the number of moles does not change during reaction, that is $a = b$, the reaction composition path is a straight line parallel to the side A B of the triangular diagram. Also plotted are the phase-solubility curves and equilibrium tie lines. If saturation cannot be achieved, then for an approximate solution the equilibrium solubility data can be replaced by effective solubility values.

Batch Systems

For the batch process the rate equation is

$$-\frac{dn_A}{dt} = k\, n_{A2} - k_1\, n_{B2}$$

or

$$-\frac{dx_A}{dt} = \frac{n_{T2}}{n_T}(kx_{A2} - k_1 x_{B2})$$

$$[1 - x_A(1 - \frac{b}{a})]$$

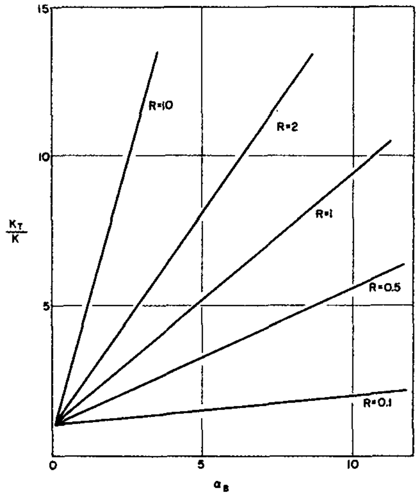

Fig. 3. Effect of the product coefficient αB and *R* on the equilibrium conversion $A \rightleftarrows B$.

and

$$dt = \frac{-dx_A \frac{n_T}{n_{T2}}}{(kx_{A2} - k_1 x_{B2})[1 - x_A(1 - b/a)]} \qquad (6)$$

where k and k_1 are the rate constants for the forward and backward reactions.

For each point T on the reaction composition path the values x_A, x_{A2}, and x_{B2} can be obtained directly from the diagram by drawing the tie line going through the point T. Furthermore the ratio n_T/n_{T2} is found by measuring the lengths $\overline{T_1T_2}$, $\overline{T_1T}$ and substituting in the relation $\overline{T_1T_2}/\overline{T_1T} = n_T/n_{T2}$. The quantity

$$\frac{n_T/n_{T2}}{(kx_{A2} - k_1 x_{B2})\{1 - x_A[1 - (b/a)]\}}$$

in (6) can then be plotted vs. x_A and a graphical integration performed for t as a function of the concentration x_A. The calculated curve $t = f(x_A)$ is drawn for convenience on Figure 1.*

CSTR Systems

The reversible first-order reaction $A \rightleftharpoons 2B$ will again be taken to illustrate the method of design for concurrent, crosscurrent, and countercurrent arrangements of continuous stirred-tank reactors. Only the concurrent procedure will be given in detail here.

Concurrent arrangement. The reaction composition path is calculated as in the batch reaction by the use of Equations (3), (4), and (5) and plotted with the physical equilibrium curves (Figure 2).

The molal balance for component A in both phases around the i^{th} stage is

$$F_{(i-1)}\, x_{A(i-1)} = F_i\, x_{Ai} + n_{Ti2}(k\, x_{Ai2} - k_1\, x_{Bi2}) \qquad (7)$$

From the initial conditions and solvent balance $F_i = [(F_o x_{So})/(x_{Si})]$, and since x_{Si} is readily found from the solubility plot when x_{Ai} is known, F_i can be calculated as a function of x_{Ai}. For each point T on the reaction composition path x_{Ai2} and x_{Bi2} are located from the corresponding tie line T_1TT_2. The quantity n_{Ti1}/n_{Ti2} is determined from

$$\frac{n_{Ti1}}{n_{Ti2}} = \frac{1}{\epsilon}\frac{F_{i1}}{F_{i2}} = \frac{1}{\epsilon}\frac{\overline{TT_2}}{\overline{T_1T}}$$

where ϵ depends on the operating conditions (*7*). With n_{Ti1}/n_{Ti2} known, n_{Ti2} is calculated from the stage-reactor volume V and the molar volumes v_A, v_B, and v_S, since

$$n_{Ti1} + n_{Ti2} = \frac{V}{x_{Ai}v_A + x_{Bi}v_B + x_{Si}v_S} \qquad (8)$$

Then two operating lines

$$f_1(x_{Ai}) = F_i\, x_{Ai} \qquad (9)$$

and

$$f_2(x_{Ai}) = F_i\, x_{Ai} + n_{Ti2}(kx_{Ai_2} - k_1 x_{Bi_2}) \qquad (10)$$

may be plotted on the triangular diagram (Figure 2†). A step-by-step graphical determination of the number of stages, expressing the equality $f_1[x_{A(i-1)}] = f_2(x_{Ai})$, is then made (*3*).

The mixed effluent concentrations are shown for the first three stages. On this graph the compositions of each effluent phase are easily read by draw-

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* Figure 1 is based on the following data: $k = k_1 = 0.1$, $x_{So} = x_{Ao} = 0.5$, $x_{Bo} = 0$; $a = 1$, $b = 2$. The equilibrium conversion of 33.3% in a single-phase process (point E) is increased to 39.0% in this extractive-reaction process (point E'). Note also that the equilibrium (infinite time) conversion of the single-phase process can be obtained by the extractive-reaction process by the use of a finite reaction time of 11.

† Figure 2 was prepared with the following data: $k = 10^{-1}$, $k_1 = 2\cdot10^{-2}$, $v_A = v_B = v_S$, $V/v_A = 10$, $\epsilon = 1$, $F_o = 1$, $x_{Ao} = x_{So} = 0.5$, and $x_{Bo} = 0$.

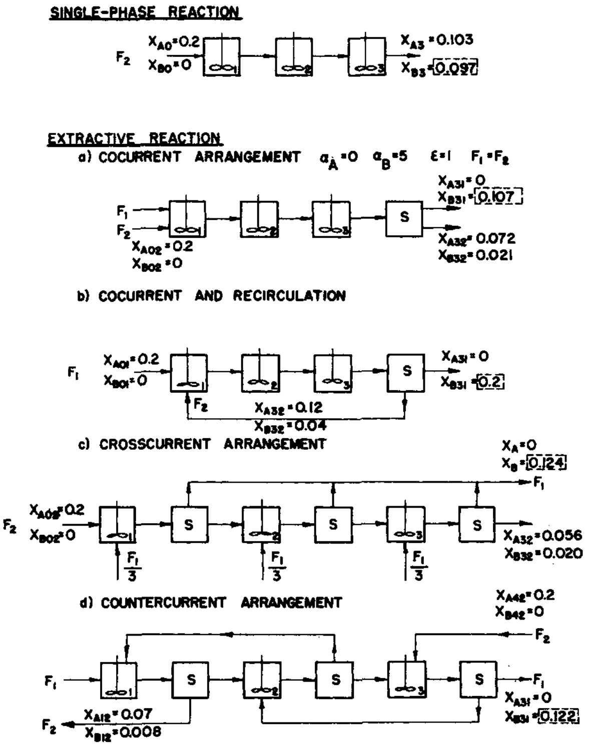

Fig. 4. Influence of the arrangement of a CSTR system on the conversion obtained. Reaction $A \overset{k}{\underset{k_1}{\rightleftarrows}} B$ with $k = k_1 = 0.1$. Separators are identified by S.

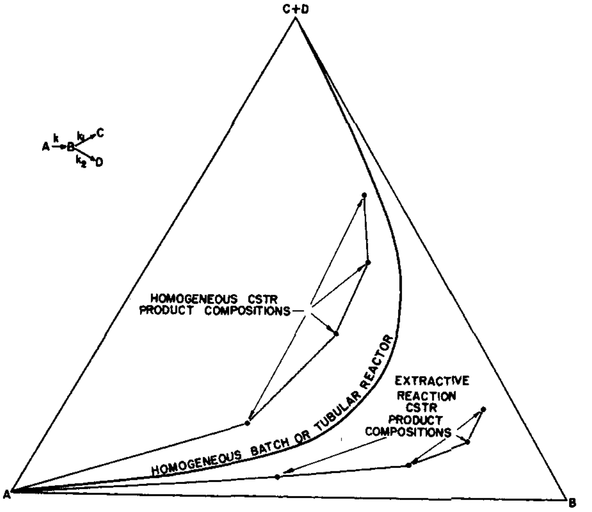

Fig. 5. Comparison of homogeneous and extractive reaction performance for a complex reaction.

ing the tie lines through the points on the reaction composition path.

If the number of moles does not change during the reaction, $F_i = F_{(i-1)} = F_o$ and the operating line $f_1(x_{Ai})$ is straight.

As mentioned before, if the reactive phase is recirculated, a trial-and-error procedure is necessary.

Crosscurrent arrangement. The procedure used for the concurrent design must be repeated for each stage of the crosscurrent arrangement. The feed to each stage is calculated by first adding the reactive-phase stream from the preceding stage to the stream of fresh solvent and then determining the reaction composition path and operating lines as before to get the outlet stream compositions.

Countercurrent arrangement. As in the two-solvent case an over-all trial-and-error procedure is required for countercurrent design if, as usual, the two necessary boundary conditions are not given at the same end of the reactor chain. Furthermore for each successive stage an additional trial-and-error solution is required, since only one stream going in and one going out of the reactor are known.

ADVANTAGES OF THE EXTRACTIVE REACTION

In the case of an extractive reaction the emphasis is on affecting the conversion of a reaction. The following discusses briefly how this effect can be obtained for some typical reversible and complex reactions.

Reversible Reactions

The usual equilibrium constant K for a reversible reaction $A \rightleftarrows B$ occurring in a single-phase system is

$$K = \frac{x^*_B}{x^*_A}$$

In the case of an extractive reaction in a batch or concurrent CSTR arrangement, three equilibrium constants can be considered:

$$K_T = \frac{x^*_{BT}}{x^*_{AT}},\ K_1 = \frac{x^*_{B1}}{x^*_{A1}},$$

$$\text{and } K_2 = \frac{x^*_{B2}}{x^*_{A1}} = K$$

Hence for a dilute two-solvent, two-phase system

$$K_T = \frac{\alpha_B R + 1}{\alpha_A R + 1} K$$

and

$$K_1 = \frac{\alpha_B}{\alpha_A} K$$

In practice α_A must be small and α_B large to obtain a large value of K_T, that is a high conversion. The ratio K_T/K for various values of R and α_B, when one assumes $\alpha_A = 0.2$ as an example, is shown in Figure 3.

Such simple relations cannot be obtained for crosscurrent and countercurrent arrangements. However in Figure 4 the performance of several arrangements are compared with the same feed used, F_2, $x_{Ao2} = 0.2$, and the same reactor volumes per stage for the reaction $A \overset{k}{\underset{k_1}{\rightleftarrows}} B$, with $k = k_1 = 0.1$, $\alpha_A = 0$, $\alpha_B = 5$, $\epsilon = 1$, and $F_1 = F_2$. Only separations and streams of solvent are added when necessary; then the residence times of the reactive phase vary for each case, the values of $k\,n_{T2}/F_2$ being respectively 1, ½, ½, ¾, and ½ for the single-phase, concurrent, concurrent with recirculation, crosscurrent, and countercurrent arrangements. It can be seen by comparing the final effluent concentrations (shown in dotted boxes) in this example that the conversion for a reversible reaction can be markedly increased by using an extractive reaction process rather than a homogeneous system.

Complex Reactions

It is readily understood that for the competing reaction $A \begin{array}{l} \rightleftarrows B \\ \rightleftarrows C \end{array}$ the conversion of A to B will be increased if an extractive-reaction process is used, where $\alpha_B > \alpha_C$. Likewise for the reaction $\begin{cases} A \rightarrow B + C \\ A + C \rightarrow D \end{cases}$ the extractive-reaction process will give a better conversion to B if $\alpha_C > 1$. Thus for many complex reactions increased conversions to desired product can be obtained if solvent systems having favorable partition coefficients can be found. This concept has not yet been used industrially as widely as the potential gains in yield would seem to warrant. Certainly broad basic studies on solubility relationships and separation properties are needed to aid in the search for suitable solvents.

As a numerical example the unidirectional reaction $A \xrightarrow{k} B \begin{array}{l} \xrightarrow{k_1} C \\ \xrightarrow{k_2} D \end{array}$ will be considered, for which analytical relations for the design of a homogeneous CSTR system have already been given in a preceding paper (*11*). In Figure 5 the homogeneous and extractive reaction operations are compared for this reaction where $k = 0.1$, $k_1 = k_2 = 0.02$, $F_1/F_2 = \epsilon\, n_{T1}/n_{T2} = 1$, $\epsilon = 1$, $\alpha_A = 0$, and $\alpha_B = 5$, α_C and α_D having any values. In all cases the initial concentrations of A in the reactive phase is 1 mole/liter, with the concentrations of B, C, and D being zero. From the plot it is seen that in this case the maximum conversion of A to B is 41% for the homogeneous CSTR system and is increased to 76% by the use of an extractive reaction CSTR process.

Comments on Reactor Selection

Some general remarks can be made regarding the choice of the best reactor arrangement to be used for an extractive reaction. Of course the choice between a batch or a continuous system will often be determined by the scale of production required; however the degree of conversion of raw material to the desired product is most often of critical importance and will largely determine the choice. The selection of a batch or tubular process vs. the several CSTR arrangements for single-phase operations has been discussed previously (*11*) and is not repeated here. If for a given homogeneous reaction this analysis shows that a single-phase batch or tubular reactor will yield a higher conversion than a CSTR design, this advantage of the batch reactor will generally be retained in the case of an extractive-reaction process. And if a CSTR design yields the better conversion in the homogeneous process, it will also do so in the two-phase process.

The concurrent CSTR arrangement can nearly always be employed, even though reactant solubilities in the solvent are not low and even though phase separation is difficult, since it has the advantage of requiring only one phase separator at the end of the chain; however the obtained conversion will be generally inferior to that obtainable from other CSTR arrangements. The crosscurrent CSTR arrangement can give good conversions when the partition coefficients of the reactants are relatively small; when they are not, an important part of the reactants will leave the system with the solvent phase, and in the absence of efficient recovery a poor utilization of the reactants will result. The countercurrent CSTR arrangement will generally give high conversions whenever part of the reactants can be fed in the solvent stream.

Of course when recirculation of the reactive phase is possible, a better utilization of the reactants and a higher conversion will generally result. In such cases the recycle stream of reactive phase can go through a CSTR or tubular homogeneous reactor before re-entering the extractive reaction system.

CONCLUSIONS

In this and in a previous paper several aspects of the extractive reaction process have been considered. The complications arising from the use of an additional solvent will often be unimportant in comparison with the gains in conversion obtained. The equation derived for extractive reaction are applicable with very few modifications, even when the reactions take place in both phases. A basic asumption is that physical equilibrium exists between the phases. This condition is most readily met in batch or CSTR operations where high levels of agitation are more easily provided than in column or tubular apparatus. It should also be noted that the factor ϵ can advantageously be varied to affect widely the phase ratio within the reactor (7).

An experimental study of a highly agitated reacting system would amount primarily to a verification of physical equilibrium between the phases, of the reaction kinetics of the system studied, and of the presence or absence of important interfacial effects, rather than being a verification of the above basic theory. Each of the first two processes will usually be best studied independently. In a subsequent paper systems where both mass transfer and chemical reaction rates are important will be considered and the experimental studies reported.

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NOTATION

$A,B,C,D \ldots S$ = components A, B, C, $D \ldots$ and solvent S
a,b,c,d = stoichiometric coefficients
F = total molar rate of flow, moles/min.
F_1,F_2 = molar rates of flow for phase 1 or 2, moles/min.
K = equilibrium constant
k,k_1,k_2 = reaction-rate constants
M = number of components taking part in the reaction
M' = number of components playing a role in the kinetics
m = number of independent variables
n = number of moles
n_{T1} = total number of moles in the extractive phase
n_{T2} = total number of moles in the reactive phase
R = ratio of the total number of moles in the extractive phase to the total number of moles in the reactive phase, n_{T1}/n_{T2}
S and S' = number of independent stoichiometric relations between the M or the M' components
t = time, min.
V = volume of the reactor
x_A = mole fraction of component A in the system = $n_{A1}+n_{A2}/n_T$
x_{A1} = mole fraction of component A in the extractive phase = n_{A1}/n_{T1}
x_{Ai1} = mole fraction of component A in the extractive phase = n_{Ai1}/n_{Ti} of the i^{th} reactor stage
α_{A1} = partition coefficient for component A, x_{A1}/x_{A2}
ϵ_i = factor relating the phase ratio in a stage to the effluent flow rates, $F_{i1}/F_{i2} = \epsilon_i R_i$, i^{th} stage

Subscripts

$A,B,C \ldots S$ = components A, B, $C \ldots$ or solvent S, respectively
T = total mass or total moles in either or both phases
o = initial conditions
$1,2,3 \ldots m \ldots M$ = components 1, 2, $3 \ldots M$ (only subscripts of x)
1,2 = extractive or reactive phase, respectively
$i,(i-1)$, or N = i^{th}, $(i-1)^{th}$, or N^{th} stage of the chain

Superscripts

$*$ = chemical equilibrium conditions

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