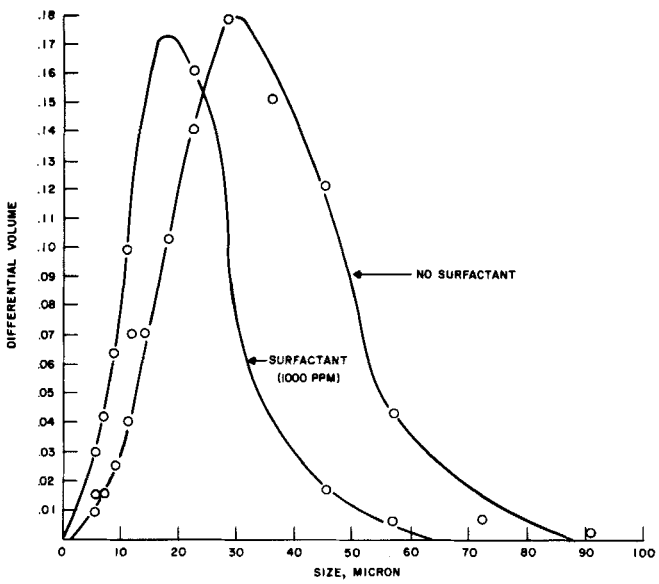

Fig. 3. Coulter counter size distributions of gypsum particles obtained from slurries with and without surfactant.

Ting and Luebbers (1957) postulated that the solid particles in a slurry form clusters or packings whose structures may be very complicated for arbitrary size distributions. Viscosity rises with increase in solid level due to occlusion of fluid in the solid structures. The probable mechanism of the influence of the surfactant is through the lubrication of the solid-liquid interface brought about by adsorption of the surfactant molecules. In other words, the surfactant molecules interfere with the packing structures and tend to increase the degree of fluidity in the suspension. In a control experiment, 60-80 mesh glass beads were suspended in phosphoric acid and the viscosities measured as a function of levels of solids and of the surfactant. No change in slurry viscosity was observed. To confirm the postulate of surface adsorption, size distribution data were obtained of the gypsum particles from both suspensions. As shown in Figure 3, the differential mass distribution measured by a Model TAII Coulter counter is shifted toward the low size for the distribution obtained from the slurry with the surfactant. Thus the formation of the solid clusters was inhibited by the action of the surfactant used in this study, as a result of which the slurry viscosity dropped.

CONCLUDING REMARKS

Following conclusions were made in the present study:

1. Viscosities of gypsum and hemihydrate slurries in wet phosphoric acid increases rapidly with the solids volume fraction, at all temperatures. Ting and Luebbers' (1957) derivation leading to Equation (3) is also valid for wide distributions with arbitrary shapes of crystals.
2. Viscosity data are well correlated by plotting x_v vs. $(\mu - \mu_0)/\mu$, and the characteristic constant $x_{v,\infty}$ is obtained from the slope of the corresponding graph.
3. The surfactant used reduced the viscosity of the phosphoric slurries significantly, presumably by facilitating the flow of solid particles past the liquid. At least in the present case, the reduction of slurry viscosity was brought about by a reduction in dominant particle size, by deagglomeration.

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NOTATION

x_v = volume fraction of solid
$x_{v,\infty}$ = volume fraction of solid in suspension for which the viscosity tends to infinity
μ = apparent viscosity measured by Brookfield viscometer, cp
μ_o = viscosity of liquid
μ_{rel} = μ/μ_o
μ_{sp} = $(\mu - \mu_o)/\mu_o$

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Micromixing Effects on Multiple Steady States in Stirred-Tank Reactors

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Occurrence of multiple steady states in chemical reactors has been studied extensively in the last two decades, and the progress made in this area has been reviewed by Perlmutter (1972), Schmitz (1974), and Luss (1976). The problem of steady state multiplicity in isothermal reactors which in general may occur for rate expressions exhibiting a maximum at some intermediate level of reactant concentration also received attention (Denbigh et al., 1948; Matsuura and Kato, 1967; O'Neil, 1971; Bruns et al., 1973). Most of these studies investigated the behavior of an ideal stirred-tank reactor which was presumed perfectly mixed on molecular level, that is, at maximum mixedness conditions. Based on this model, uniqueness criteria and regions of multiplicity were evaluated (Matsuura and Kato, 1967; O'Neil et al., 1971). However, it is well known that reactor performance is affected not only by the residence time distribution (RTD) but also by the fluid's state of aggregation and by the micromixing paths

which accomplish the transition from segregation by age to segregation by life expectation (Weinstein and Adler, 1967; Nishimura and Matsubara, 1970). Performance of isothermal reactors with fixed RTD has been evaluated at the two micromixing extremes of segregated flow and maximum mixedness (Douglas, 1964) and at intermediate levels of micromixing (Bischoff, 1966; Fan et al., 1971; Dohan and Weinstein, 1973). Surprisingly, the effect of micromixing on performance of isothermal reactors that may exhibit multiple steady states has not been considered, although it can be expected that this effect will be most pronounced in such systems. In the only previous study of the micromixing effects on multiple steady states in adiabatic chemical reactors (Yang et al., 1974), considerable effects were reported. Otherwise, the important micromixing effects which are related to the turbulence field in the system were completely ignored in other studies of steady state multiplicity and stability.

It is known and documented that well-mixed continuous flow stirred-tank reactors (CSTR) exhibit close to an exponential RTD but are not perfectly and instantaneously mixed on molecular level, since tracer concentration fluctuations are always detected at various points in the reactor (Evangelista et al., 1969; Khang and Levenspiel, 1976). This implies that the reactor is never in maximum mixedness conditions and that the actual degree of segregation and micromixing patterns are determined by the state of the fluid and the intensity and scale of turbulence. Modeling such reactors by ideal stirred-tank equations oversimplifies physical reality. It is the purpose of this paper to demonstrate that neglecting the micromixing effect in stirred-tank reactors may lead to incorrect mapping of the region of possible multiple steady states.

DEVELOPMENT

The dimensionless design equation for an ideal stirred-tank reactor in the case of a self-inhibited rate expression is given by Equation (1):

$$\frac{1}{Da}(X_o - X) - \frac{X}{(1+X)^2} = 0 \qquad (1)$$

The plot of the dimensionless rate against dimensionless concentration is presented in Figure 1. Clearly the reactor steady states, given by solutions of Equation (1), are graphically represented by the intersections of the straight line (of slope $-Da^{-1}$ and intercept on the abscissa X_o) with the nonlinear rate curve. The criteria for uniqueness (Perlmutter, 1972) require either that the slope of the rate curve be larger than the slope of the straight line [Equation (2)] or, more conservatively, that the minimum slope of the rate curve, that is, the slope at inflection point, be larger than the slope of the straight line [Equation (3)]:

$$\frac{d[\bar{r}(X)]}{dX} > -\frac{1}{Da} \Rightarrow X_o < 8 \qquad (2)$$

$$\min \frac{d[\bar{r}(X)]}{dX} > -\frac{1}{Da} \Rightarrow Da < 27 \qquad (3)$$

The first criterion leads to unique steady states of relatively high conversion. However, for feeds of fixed inlet concentration $X_o > 8$, one can map the region of possible multiple steady states. Multiplicity may occur only in a strip indicated in Figure 1 between two parallel lines of slope $-Da^{-1}$ which are tangent to the rate curve. The intercepts of these lines on the abscissa determine the region of dimensionless feed concentrations $X_o^l \leq X_o \leq X_o^u$ for which multiple steady states are possible. For the example of Figure 1 and Damkohler number of 52.63, the bifurcation points are found by requiring that X_b satisfies both Equation (1) and its first derivative.

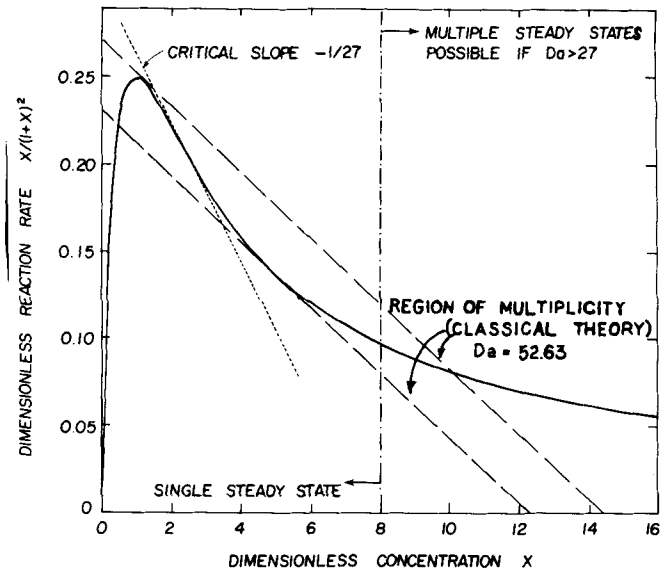

Fig. 1. Possible steady states in an ideal stirred-tank reactor.

The bifurcation points occur at the values of X of 4.8976 and 1.2032. The first value corresponds to the lower limit of the inlet concentration $X_o^l = 12.3084$ and the second one to the upper limit $X_o^u = 14.2488$. For any inlet concentration between these two values, classical theory predicts three possible steady states and guarantees one steady state for all X_o's on either side of this interval.

Micromixing effects in a well-mixed stirred-tank reactor (reactor of exponential residence time distribution) can be accounted for by a number of models (Nishimura and Matsubara, 1970). For illustrative purposes the consecutive segregated maximum mixedness model (CSMM) (Weinstein and Adler, 1967; Nishimura and Matsubara, 1970) is used in this paper. The basic assumption of the model is that the fluid in the reactor can be divided in two parts. All the fluid elements of age younger than α^* (which is numerically equal to θ^*) are in segregated flow condition; all the elements older than α^* are in maximum mixedness condition. This implies that all the fluid elements in the outflow that have residence times less than θ^* have been surrounded by elements of the same age, have reacted only in segregated flow conditions, and are mixed with elements of different ages at the outlet only. Fluid elements in the outflow of residence time larger than θ^* have spent time θ^* in segregated flow and $\theta - \theta^*$ in maximum mixedness condition.

The degree of segregation (Danckwerts, 1958) in terms of model parameters is now given by

$$J = 1 - \frac{\overline{\mathrm{VAR}(\alpha_i)}}{\overline{\mathrm{VAR}(\alpha)}} = 1 - e^{-\theta^*} \qquad (4)$$

Conversion in the outlet can be calculated from

$$1 - x = \frac{1}{X_o}\int_o^{\theta^*} X_{\mathrm{agg}}(\theta)\, e^{-\theta}\, d\theta + e^{-\theta^*}\frac{X_{ms}(\theta^*)}{X_o} \qquad (5)$$

$$-\frac{dX_{\mathrm{agg}}}{d\theta} = \frac{Da\, X_{\mathrm{agg}}}{(1+X_{\mathrm{agg}})^2} \qquad (6)$$

$$\theta = 0; \quad X_{\mathrm{agg}} = X_o \qquad (6a)$$

$$\frac{1}{Da}(X^* - X_{ms}) - \frac{X_{ms}}{(1+X_{ms})^2} = 0; \quad \theta^* \leq \lambda \leq \infty \qquad (7)$$

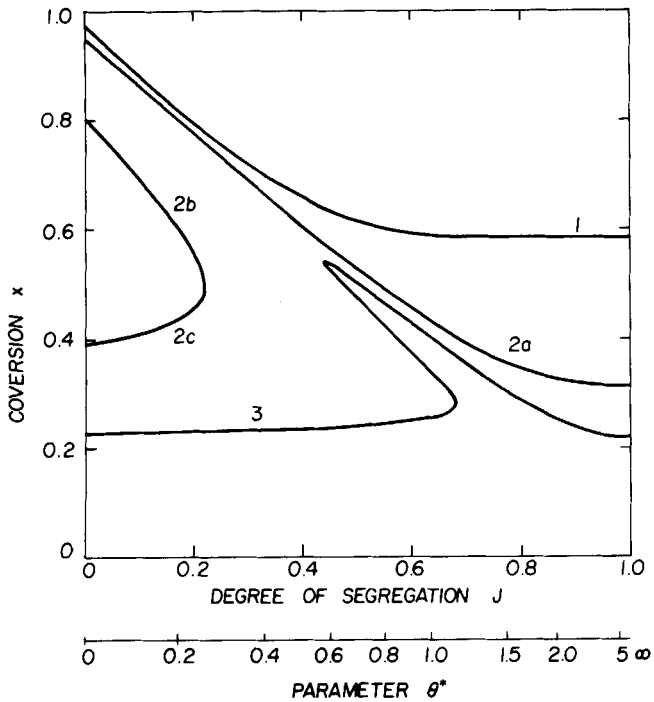

Fig. 2. Micromixing effects on conversion in a stirred-tank reactor [$Da = 52.63$; 1. $X_o = 8$; 2. a, b, c, $X_o = 13.2$; 3. $X_o = 16$].

where

$$X^* = X_{agg}(\theta^*) \tag{7a}$$

The first term on the right of Equation (5) represents the contribution of the segregated portion of the reactor; the second term is the contribution of the maximum mixedness section. Equation (6) shows how concentration changes in an aggregate in segregated flow, and Equation (7) represents the performance of the maximum mixedness section of the reactor.

Integration of Equation (6) leads to

$$\theta = \frac{1}{Da}\left[\ln\frac{X_o}{X_{agg}} + 2(X_o - X_{agg}) + \frac{1}{2}(X_o^2 - X_{agg}^2)\right] \tag{8}$$

Since X_{agg} cannot be obtained as an explicit function of θ, Equation (8) is used to perform a change of variables in the integral of Equation (5), leading to

$$1 - x = \frac{\exp\left\{-\dfrac{2X_o + X_o^2/2}{Da}\right\}}{Da\, X_o^{(1+1/Da)}} \int_{X^*}^{X_o} X^{\frac{1}{Da}} (1+X)^2 \exp\left[\frac{2X + X^2/2}{Da}\right] dX + e^{-\theta^*}[X_{ms}(\theta^*)/X_o] \tag{9}$$

where X^* is the dimensionless concentration in an aggregate at time θ^*, and thus X^*, θ^* also satisfy Equation (8).

The results are computed by using the Romberg subroutine for the calculation of the integral in Equation (9) with absolute error less than 10^{-9}, while the roots of Equation (7) were found by the Newton-Raphson method. The results are presented in Figure 2 for $Da = 52.63$ and three values of the dimensionless initial concentration ($X_o = 8$; 13.2; 16).

DISCUSSION AND CONCLUSIONS

For dimensionless inlet concentrations of $X_o = 8$ and $X_o = 16$, a unique steady state is predicted by the classical theory based on an ideal stirred-tank reactor, since these X_o's lie outside the strip of multiple steady states as seen in Figure 1. Three steady states are expected at the maximum mixedness condition ($J = 0$) for $X_o = 13.2$.

Figure 2 clearly indicates the potential importance of the micromixing effects. The conversion for a unique steady state ($X_o = 8$) changes considerably when the degree of segregation varies from 0 to 1. Multiple steady states possible at conditions of maximum mixedness ($J = 0$) for $X_o = 13.2$ are not any more realizable if J increases above a certain value ($J = 0.22$ for the CSMM). Most importantly, unexpectedly high conversions and multiple steady states may occur over a range of J's in the case of $X_o = 16$ in spite of the fact that only one steady state of relatively low conversion is possible at maximum mixedness conditions as predicted by the classical theory.

Micromixing cannot be described by a single parameter such as the degree of segregation and different models of micromixing lead to different predictions of reactor performance and steady state multiplicity (Dudukovic, 1977). The important point is that the micromixing patterns do considerably affect the region of possible multiple steady states and may give rise to multiplicity which cannot be predicted by classical theory of ideal stirred-tank reactors. This implies that the performance of a CSTR can only be truly estimated if the complete description of micromixing is known, that is, if the proper model and parameters are chosen and related to the turbulence field in the reactor.

NOTATION

C = reactant concentration, (mole/l)
$Da = k\bar{t}$ = Damkohler number, dimensionless
J = degree of segregation, dimensionless
k = reaction rate constant, s^{-1}
K = constant, $(mole/l)^{-1}$
$\bar{r}$ = reaction rate, dimensionless
$\bar{t}$ = reactor mean residence time, s
$\overline{VAR(\alpha_i)}$ = weighted average of the variance of ages within all points of the system, dimensionless
$\overline{VAR(\alpha)}$ = variance of all ages of the fluid in the system, dimensionless
x = reactant fractional conversion, dimensionless
$X = KC$ = reactant concentration, dimensionless
X_{agg} = reactant concentration in a fluid aggregate at time θ, dimensionless
X_o = reactant inlet concentration, dimensionless
X^* = reactant concentration in the maximum mixedness section of the CSMM, dimensionless
X_o^l = lower bound on the range of initial concentrations within which multiple steady states are possible, dimensionless
X_o^u = upper bound in the concentration range that allows multiple steady states, dimensionless
α = age of a fluid element in the reactor dimensionless
α^* = age of fluid which divides the reactor contents into two portions in the CSMM, dimensionless
$\theta = t/\bar{t}$ = residence time, dimensionless
θ^* = parameter of the CSMM, dimensionless

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Mass Velocity Measurement in Steam-Water Flow by Pitot Tubes

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Pressure, temperature, void fraction, and mass velocity must be measured in transient steam-water flow experiments related to reactor safety. Void fraction and mass velocity measurement techniques are still being developed. Multibeam γ ray attenuation techniques to measure void fraction (Banerjee et al., 1976; Heidrick et al., 1976) appear promising for practical applications. Mass velocity is more difficult to measure, and many devices have been used. Of these, Pitot tubes are particularly attractive because they are rugged and stand up well in high pressure steam-water environments.

Banerjee et al. (1976) have measured mass velocity in transient steam-water flow with Pitot tubes which were not directly calibrated. Reproducible results and good response to flow transients were obtained over several months operation. Pitot tubes have also been used by Anderson and Mantzouranis (1960), Adorni et al. (1961), Gill et al. (1963), Delhaye (1966), and Dzakowic and Dix (1969) to investigate steady gas-liquid flow and by Dussourd and Shapiro (1955) and Dalmon and Lowe (1957) for gas-solid flow. Generally, reasonable agreement with input flow was obtained by integrating the total phase flow across the channel.

To develop the technique further, Pitot tubes should be directly calibrated in steady and transient steam-water flows covering a wide range of mass velocities, void fractions, and pressures. To interpret the measurements, simultaneous void fraction measurements are required. This note describes the first stage of such a program. The main objective was to determine whether it was feasible to use Pitot tubes to measure mass velocity in high pressure, high mass velocity steam-water flows.

EXPERIMENTS

To determine the feasibility of measuring cross section averaged mass velocity with Pitot tubes, experiments were done in the facility shown in Figure 1. The flow rate, temperature, and pressure of the hot water and superheated steam were monitored before they entered the mixer. The mixer consisted of a single pass shell and tube heat exchanger with one end cut off. The steam and water flowed concurrently along the heat ex-

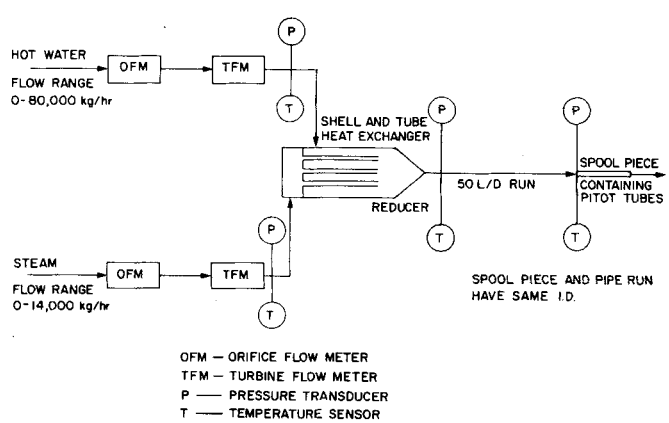

Fig. 1. Schematic of experimental facility.