binary mixture (fructose-water, Figure 2) since α depends only on the values of C_2 and b_i, where C_2 is defined as the ratio of dead volume of the bottom reservoir to the displacement.

Chen and Hill (1971) have shown that there are three possible regions of pump operations. Regions 1, 2, and 3, depending on the relative magnitudes of penetration distances L_{1i} and L_{2i}, and the height of the column h. As long as

$$b_g < \phi_B \leq b_f \quad \text{and} \quad L_{2f} \leq h \qquad (2)$$

for the continuous pump and

$$\left(\frac{2b}{1-b}\right)_g < \phi_B \leq \left(\frac{2b}{1-b}\right)_f \quad \text{and} \quad L_{2f} \leq h \quad (3)$$

for the semicontinuous pump, the operation is in Region 1 for fructose and Region 2 for glucose. At steady state ($n \rightarrow \infty$) fructose appears only in the top product stream, but glucose would appear in both top and bottom product streams. However, as stated before, for the present study $b_g = 0$, and the glucose concentration in either top or bottom product stream is identical to that of the feed.

It should be emphasized that the performance characteristics of both continuous and semicontinuous pumps are similar in nature. The main difference between the two pumps is the difference in the loci of switching points between Regions 1 and 2 (Chen and Hill, 1971). For the continuous pump, the switching points correspond to the condition $\phi_B = b_i$. In the case of the semicontinuous pump, the condition is $\phi_B = 2b_i/(1 - b_i)$.

Figure 4 shows the effects of ϕ_T and ϕ_B on the degree of enrichment in the top product stream. ϕ_T and ϕ_B are defined as the ratios of the top and bottom product flow rates to the reservoir displacement rate. Provided that the pumps are operated in Region 1 [see Equations (2) and (3)], the top product concentration at $n \rightarrow \infty$ would be $\langle y_{TP2} \rangle_\infty / y_0 = 1 + \phi_B/\phi_T$. As ϕ_B increases, $\langle y_{TP2} \rangle_\infty / y_0$ increases. Furthermore, for a given value of ϕ_B, by adjustment of ϕ_T to an arbitrarily low value, one may obtain an arbitrarily high value of $\langle y_{TP2} \rangle_\infty / y_0$.

NOTATION

b = equilibrium parameter, dimensionless
C_1 = top reservoir dead volume/displacement, dimensionless
C_2 = bottom reservoir dead volume/displacement, dimensionless
h = column height, m
L_1 = penetration distance for hot cycle, m
L_2 = penetration distance for cold cycle, m
n = number of cycles of pump operation
Q = reservoir displacement rate, cm^3/s
R^0 = polarimeter reading, angular degree
T_1 = column temperature during upflow, °K
T_2 = column temperature during downflow, °K
y_0 = initial or feed concentration of solute, g moles/cm^3
$\langle y_{BP2} \rangle_n$ = average bottom product concentration of solute during downflow at nth cycle, g moles/cm^3
$\langle y_{TP2} \rangle_n$ = average top product concentration of solute during downflow at nth cycle, g moles/cm^3
η = concentration, g mole/cm^3
β = R^0/η
ϕ_B = bottom product volumetric flow rate over reservoir displacement rate, dimensionless
ϕ_T = top product volumetric flow rate over reservoir displacement rate, dimensionless
π/ω = duration of half cycle, s

Subscripts

f = fructose
g = glucose
i = solute i
∞ = steady state

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Further Considerations on the Danckwerts-Gillham Method for Design of Gas Absorbers

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In a recent paper, Charpentier and Laurent (1974) recall a method proposed by Danckwerts and Gillham (1966) for prediction of the effect of a chemical reaction on the overall rate of gas absorption. The aim of this note is to clarify some characteristics and limitations of such a method.

Both experiments and theory indicate there are two sets of factors in the design of absorption equipment: the physico-chemical characteristics and the hydrodynamics of the system. Any design method must be based on similarities of both.

The stirred cell model proposed by Dankwerts (1966) is used as follows: The enhancement factor is obtained experimentally both in the laboratory model and in the industrial absorber, that is, (following (Danckwerts) a packed column. This can be done by measuring both the mass transfer coefficient for absorption in a chemically reacting solution, and in a solution that has the same physical properties, but does not react with the gas. This is done both in the model and the packed column. The hydrodynamic conditions are then changed until the ratio ϕ_m/ϕ_c is equal to one, the enhancement factors ϕ_m and ϕ_c being obtained experimentally from the model and the column, respectively. It is assumed that when that condition is fulfilled, for example, $\phi_m/\phi_c = 1$, the systems are equivalent, and, repeating the experiments, a relation between the liquid flow rate in the packed column and the stirrer speed in the model can be established. Once determined, this relationship "will be permanently recorded for use by designers with the imperious condition that experiments on new liquids and gases must be done with a vessel identical in design to that used to obtain the original data" (Charpentier and Laurent, 1974).

At first glance, it may be thought that the purpose is just to find the hydrodynamic conditions where k_L, the coefficient for physical mass transfer in the model, is equal to the coefficient of the industrial apparatus (Charpentier and Laurent, 1974; Yano et al., 1973). But such a correlation could be obtained in a much easier way by performing only physical absorption experiments and without going into the problems associated with a chemical reaction in the system. Only k_{Lm} determinations would be needed since k_{1c} can be obtained in general from published correlations as observed by Danckwerts and Gillham (1966).

However, such a correlation will not give strictly the same information as the foregoing. The reason is that in industrial equipment the local values of the mass transfer coefficient vary along the whole column and the measured value is in fact the mean over the interfacial area

$$k_L = \frac{\int k_L(a)\,da}{\int da} \qquad (1)$$

$$k_L a = \int k_L(a)\,da \qquad (2)$$

Thus, the enhancement factor being a function of k_L, we may get different local values of ϕ_c at different points of the system. Given the relatively wide range of variation of reported data of mean mass transfer coefficients in packed columns (Danckwerts, 1970), it can be suspected that a similar or even a wider range of variation exists for local values of k_L.

Let us give a hypothetical example to show the effects of such a distribution:

Suppose a packed column with a measured mass transfer coefficient for physical absorption $k_L = 11 \times 10^{-3}$ cm/s. Assume now that such a value is the mean of two kinds of flow regimes; in the zones where flow is along long slow paths, assume about 50% of the interfacial area, the mass transfer coefficient is low, $k_{L1} = 2 \times 10^{-3}$ cm/s. In the other half of the interfacial area, mixing conditions prevail, and the mass transfer coefficient in zone 2 is $k_{L2} = 20 \times 10^{-3}$ cm/s. The measured value $k_{Lc} = 11 \times 10^{-3}$ cm/s is then the mean of our two hypothetical zones. On the other hand, we have an experimental model with a homogeneous distribution of mass transfer coefficient. We may think that once we find the agitation needed to obtain a value $k_{Lm} = 11 \times 10^{-3}$ cm/s, we have found a condition that corresponds to our packed column. But let us see what happens when we try an absorption with a second order chemical reaction.

Let us accept that the enhancement factor is given accurately enough by

$$\phi = \frac{\gamma\sqrt{(\phi_\infty - \phi)/(\phi_\infty - 1)}}{\tanh\left(\gamma\sqrt{(\phi_\infty - \phi)/(\phi_\infty - 1)}\right)} \qquad (3)$$

$$\text{being} \quad \gamma = \sqrt{k_2 C_{BL} D_A}/k_L \qquad (4)$$

a Damköelher number and

$$\phi_\infty = 1 + \frac{D_B\,C_{BL}}{Z\,D_A\,C_{Ai}} \qquad (5)$$

the enhancement factor for an instantaneous second-order reaction. Let us assume that the operating conditions are such that $\phi_\infty = 20$ and

$$\sqrt{k_2 C_{BL} D_A} = 0.1 \text{ cm/s}$$

When performing the experiments on the laboratory model, we will find the following:

$$\gamma_m = 0.1/11 \times 10^{-3} = 9.09$$

and from Equation (3) we get

$$\phi_m = 7.4$$

The mass transfer coefficient, including the chemical reaction, will be

$$k'_{Lm} = k_{Lm}\,\phi = 81.43 \times 10^{-3} \text{ cm/s}$$

The assumption that an equality of physical mass transfer coefficient is enough to establish equivalence for mass transfer with chemical reaction would lead us to the prediction of the same γ and the same ϕ for the packed column. But let us see what really occurs. In the first, slow paths low mass transfer rate zone, we get $k_{L1} = 2 \times 10^{-3}$ cm/s, $\gamma_1 = 50$, $\phi_1 = 17.63$, $k'_{L1} = 35.26 \times 10^{-3}$ cm/s.

In the second well agitated zone, $k_{L2} = 20 \times 10^{-3}$ cm/s, $\gamma_2 = 5$, $\phi_2 = 4.51$, and $k'_{L2} = 90.20 \times 10^{-3}$ cm/s.

The overall mass transfer coefficient for the packed column will be

$$k'_{Lc} = 0.5\,k'_{L1} + 0.5\,k_{L2} = 62.73 \times 10^{-3} \text{ cm/s}$$

We have obtained, based on reasonable data (except for the excessive simplification of a sharp transition between both zones), a deviation of 23%.

That would be the price of accepting the fact that equality in mean physical mass transfer coefficients is a sufficient condition for similarity between the laboratory model and the industrial equipment.

A correlation between k_{Lm} and k_{Lc} is thus not enough. This is, in fact, the contribution of the Danckwerts method, which seeks a correlation rather between ϕ_m and ϕ_c. See, for instance, the poor correlation of k_{Lm} and k_{Lc} in the data of Jhaveri and Sharma (1969) and compare with the excellent correlation of their data of ϕ_m and ϕ_c.

It can be said on the basis of available experimental data that the stirred cell proposed by Danckwerts and Gillham (1966) has the merit of giving a distribution of local mass transfer coefficients that is equivalent in its mass transfer characteristics to a packed column. However, the whole procedure can be simplified if we have an expression of the distribution of local mass transfer coefficients in a packed column. Some ways to obtain such relationships have been proposed before (Ronco and Merchuk, 1966; Porter, 1966; Merchuk and Ronco, 1970; Merchuk et al., 1970). Unfortunately, not much attention has been paid to them in the technical literature. From these models, it can be seen that the expected deviation from values of ϕ calculated by taking k_L as a constant are small for first-order reactions so that any laboratory model whose range of k_L is the same as that of a packed column will represent it satisfactorily in the case of a first-order kinetic. Not to speak about the case of a very rapid first-order or pseudo first-order reaction, where $k_L' = \sqrt{k_2 C_{BL} D_A}$, and k_L has no influence on the mass transfer rate.

In the case of a second-order reaction, however, the influence may be much more important, and careful experiments have been performed by Merchuk et al. (1970) in order to determine the distribution function.

The consideration of the distribution of the local value of k_L (Merchuk et al., 1970) allows us to predict small positive deviations of ϕ in the case of a first-order reaction, and negative deviations for higher reaction orders. Indeed, that is the tendency which can be seen in the data by Jhaveri and Sharma (1970) (Figure 1).

Even if the influence of the distribution of the local mass transfer coefficients is not too important from a practical point of view, since the errors that result from not considering such distribution are not too big (about 15% in the only reported data, Merchuk et al., 1970), the understanding of the phenomenon is important from a more basic point of view and explains why the Danckwerts and Gillham's method is better than a simple correlation between mass transfer coefficients of a model and those of industrial equipment.

NOTATION

a = interfacial area per unit volume, cm^{-1}
CA_i = concentration of dissolved gas at interface in equilibrium with gas at interface, mol/cc
C_{BL} = concentration of reactant B in the bulk of the liquid, mol/cc
D_A = diffusivity of dissolved gas, cm^2/s
D_B = diffusivity of reactant B, cm^2/s
k_L = liquid film mass transfer coefficient cm/s
k_L' = liquid film mass transfer coefficient, with chemical reaction, cm/s
k_2 = second-order rate constant for reaction of A, cc/mol s
z = number of moles of reactant B reacting with each mole of solute A

Greek Letters

γ = Damköelher number, given by Equation (4), dimensionless
ϕ = enhancement factor for an instantaneous second-order reaction, dimensionless

Subscripts

c = packed column, industrial apparatus
m = laboratory model

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Pseudo Steady State Approximation for the Numerical Integration of Stiff Kinetic Systems

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Recently Aiken and Lapidus (1974) have derived a solution approximation for stiff systems of the partitioned form

$$\dot{\mathbf{x}} = \frac{d\mathbf{x}(t)}{dt} = \mathbf{f}(\mathbf{x}, \mathbf{y}), \ \mathbf{x}(0) \tag{1}$$

$$\dot{\mathbf{y}} = \frac{d\mathbf{y}(t)}{dt} = \mathbf{w}(\mathbf{x}, \mathbf{y}), \ \mathbf{y}(0) \tag{2}$$

where y denotes the stiff variable vector and x the nonstiff variable vector. The solution was given in terms of zeroth-