CHROM. 15,682

LINEAR NON-EQUILIBRIUM CHROMATOGRAPHIC REACTOR WITH A FIRST-ORDER CHEMICAL REACTION

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(Received December 8th, 1982)

SUMMARY

A model is presented for a linear chromatographic reactor with a first-order reaction and three non-equilibrium processes. The following three conclusions are derived based on the Laplace transform of the reactant concentration: (1) the input–output ratio of the reactant is a function of longitudinal diffusion and interfacial diffusion in addition to the reaction rate constant; (2) moment analysis indicates that six parameters pertinent to the linear chromatographic reactor can be determined from the area ratio (or zeroth moment), and the second-order central moment as a function of flow-rate; (3) an approximation to describe the solid-phase concentration by a first-order ordinary differential equation needs a rate coefficient which depends on other parameters of the system besides the solid-phase diffusion coefficient.

INTRODUCTION

Studies of a chemical reaction in a gas chromatographic (GC) column have received attention both experimentally[1–3] and theoretically[4,5]. Because the reactant in the chromatographic column gas is present in a highly diluted state, the GC reactor is generally applied to study a first-order or a pseudo-first-order reaction. Mathematical results in the literature[6,7] usually draw the conclusion that the concentration of the reactant at the column outlet decreases exponentially with the retention time. This conclusion is valid under the assumption of an ideal chromatographic reactor (ICR)[6,7] where there is no spreading and where each reactant molecule has exactly the same retention time in the column.

A slight modification of the ICR assumption will show that the exponential-decay result is not valid: when there is longitudinal diffusion, some molecules spend less and some spend more than the average retention time. Although their average time is the retention time, the average concentration is not the concentration that corresponds to the average retention time because the output concentration at different times is weighted by different exponential factors. This effect can be seen from

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the mathematical results of Kocirik[5] and Madey *et al.*[8]. In this study, non-equilibrium effects are taken into account in a model to calculate the output concentration. Three non-equilibrium processes are included: longitudinal diffusion, solid-phase diffusion and gas–solid interfacial mass transfer.

MATHEMATICAL MODEL

Assume that the chromatographic system has a linear isotherm and that a first-order reaction takes place in both the gas phase and the stationary solid phase. Assume also that the pressure drop is small and that the diameter of the solid phase is small compared to the column diameter, so that the flow-rate, u, is constant throughout the column. Under these assumptions, the differential equations, which describe the gas-phase concentration, C, and the solid-phase concentration, q, are written as:

$$\frac{\partial C}{\partial t} + u \cdot \frac{\partial C}{\partial z} - D_L \cdot \frac{\partial^2 C}{\partial z^2} = \frac{1-\varepsilon}{\varepsilon} \cdot \frac{\partial \overset{\triangle}{q}}{\partial t} - \frac{1-\varepsilon}{\varepsilon} \cdot \lambda_s \overset{\triangle}{q} - \lambda_g C \tag{1}$$

and

$$\frac{\partial q}{\partial t} = D_s \left(\frac{\partial^2 q}{\partial r^2} + \frac{2}{r} \cdot \frac{\partial q}{\partial r} \right) - \lambda_s q \tag{2}$$

The average solid-phase concentration, $\overset{\triangle}{q}$, for spherical pellets is given by:

$$\overset{\triangle}{q} = \frac{3}{R^3} \int_0^R q(r, z, t)\, r^2\, \mathrm{d}r \tag{3}$$

Here we assumed that the gas-phase concentration does not change significantly over a distance equal to a diameter of the catalyst pellets. This assumption was discussed by Babcock *et al.*[9]. The introduction of an average concentration eliminates the radial dependence of the solid-phase concentration from eqn. 1.

The initial and boundary conditions are written as:

$$C(0,t) = f(t) \tag{4}$$

$$C(\infty,t) = 0 \tag{5}$$

$$C(z,0) = 0 \tag{6}$$

$$q(0,z,t) \neq \infty \tag{7}$$

$$q(r,z,0) = 0 \tag{8}$$

The interfacial mass transfer resistance is written as

$$\frac{\partial \overset{\triangle}{q}}{\partial t} = \frac{3k_f}{R}\left(C - \frac{q_s}{K}\right) - \lambda_s \overset{\triangle}{q} \tag{9}$$

and the solid-phase concentration, q_s, at the surface is defined as:

$$q_s\,(z,t\,) = q(R,z,t\,) \tag{10}$$

Eqn. 10 is the mathematical representation of the statements following eqn. 3.

Note that eqns. 1, 2, 9 and 10 are four linear equations that contain the four variables, C, $\overset{\triangle}{q}$, q_s and q. Taking the Laplace transform and eliminating the solid-phase concentration, we have

$$\frac{\partial^2 \tilde{C}}{\partial z^2} - \frac{u}{D_L}\cdot\frac{\partial \tilde{C}}{\partial z} - \left[\frac{p}{D_L} + \frac{\lambda_g}{D_L} + \frac{Y_T(p)}{mD_L}\right]\tilde{C} = 0 \tag{11}$$

where

$$Y_T(p) = \frac{Y_D(p)}{1 + R_F Y_D(p)} \tag{12}$$

$$Y_D(p) = \frac{3Kp}{\sigma^2}\,(\sigma \coth \sigma - 1) + \lambda_s K \tag{13}$$

$$\sigma = R\sqrt{\frac{p + \lambda_s}{D_s}} \tag{14}$$

$$R_F = R/3k_f \tag{15}$$

$$m = \frac{\varepsilon}{1 - \varepsilon} \tag{16}$$

In eqn. 11, $\tilde{C}$ represents the Laplace transform of C. Eqn. 11 is a homogeneous second-order linear differential equation. The solution is[10]

$$\frac{\tilde{C}(L, p)}{C_0} = \tilde{f}(p)\exp\left[\frac{uL}{2D_L} - L\sqrt{Y_A(p)}\right] \tag{17}$$

where $\tilde{f}(p)$ is the Laplace transform of $f(t)$, and

$$Y_A(p) = \frac{u^2}{4D_L^2} + \frac{p}{D_L} + \frac{Y_T(p)}{mD_L} + \frac{\lambda_g}{D_L} \tag{18}$$

DISCUSSION

Gas-phase concentration at the column outlet

The reaction-rate constant is usually determined through the ratio of the concentration of the reactant at the column outlet to that at the inlet of the column. It is sufficient to use the area in the chromatogram to represent the amount of reactant because the area depends linearly on the output concentration. The total amount of a reactant at the column inlet is:

$$R_{in} = \int_0^\infty f(t)\,dt = \lim_{p \to 0} \tilde{f}(p) \tag{19}$$

The second equality in eqn. 19 follows from the definition of the Laplace transform. The same method is applied to the output signal to obtain:

$$R_{out} = \lim_{p \to 0} \tilde{C}(L, p) = \tilde{f}(p = 0) \exp\left\{\frac{uL}{2D_L} - \frac{uL}{2D_L}\left[1 + \frac{4\lambda_g D_L}{u^2} + \frac{4D_L \lambda_s K}{um(1 + R_F \lambda_s K)}\right]^{1/2}\right\} \tag{20}$$

From eqns. 19 and 20, we have:

$$\ln \frac{R_{in}}{R_{out}} = -\frac{uL}{2D_L}\left\{1 - \left[1 + \left(\frac{4D_L}{uL}\right)\left(\frac{\lambda_g L}{u} + \frac{L\lambda_s K}{um(1 + R_F \lambda_s K)}\right)\right]^{1/2}\right\} \tag{21a}$$

Using a binomial expansion, we obtain:

$$\ln \frac{R_{in}}{R_{out}} = \frac{\lambda_g L}{u} + \frac{KL\lambda_s}{um(1 + R_F \lambda_s K)} \quad \text{when} \quad \frac{4D_L}{uL}\left[\frac{\lambda_g L}{u} + \frac{L\lambda_s K}{um(1 + R_F \lambda_s K)}\right] \ll 1 \tag{21b}$$

$$= \frac{\lambda_g L}{u} + \frac{R_F LK^2 \lambda_s^2}{um} + \frac{KL\lambda_s}{um} \quad \text{when, in addition,} \quad R_F \lambda_s K \ll 1 \tag{21c}$$

$$= \frac{\lambda_g L}{u} - \frac{KL\lambda_s}{um} \quad \text{when, in addition,} \quad R_F \lambda_s K \ll \frac{m\lambda_g}{K\lambda_s} \tag{21d}$$

Eqn. 21d is the expression generally used in studies of chromatographic reactors. It is valid only when both the longitudinal diffusion coefficient and the interfacial mass-transfer resistance is zero. It is interesting to note also the solid-phase diffusion coefficient, D_s, does not appear in the expressions.

Eqn. 21b is generally valid because the second term on the right-hand side is approximately equal to $\ln(R_{in}/R_{out})$, which is typically of order unity in a kinetic measurement; while the factor $4D_L/uL$, which is equal to the reciprocal of the number of theoretical plates, is smaller than 0.01 in most experimental situations[11]. Little can

be said about the conditions leading to eqns. 21c and 21d. In one of our previous papers[12], we used the correlation from Petrovic and Thodos[13]. In terms of the symbols in this paper, the correlation would read as

$$R_F = 0.934 \, R \, (1 - \varepsilon)^{-1} u^{-1} \mathrm{Re}^{0.359} \mathrm{Sc}^{0.667} \tag{22}$$

where Re and Sc are the dimensionless Reynolds and Schmidt numbers, respectively. In order to illustrate a value for R_F, we use the result of run (b) of Fig. 1 in ref. 3. For 60–80 mesh, R is $3.7 \cdot 10^{-2}$ cm. The value of ε is assumed to be 0.34. For a volumetric flow-rate of 30.8 cm³/min at 180°C, a 0.25-in. column has a superficial flow-rate of 1.62 cm/sec. The Reynolds number is 1.8×10^{-2} and the Schmidt number is 6.2. The value of R_F is $2.6 \cdot 10^{-2}$ sec. The reaction rate constant, λ_s, and the partition coefficient, K, were listed in ref. 3 for several temperatures. A value of 0.025 sec⁻¹ represents the product $\lambda_s K$ for several solvents. The product $R_F \lambda_s K$ is about $6 \cdot 10^{-4}$, which is small enough to justify eqns. 21c and 21d. For liquid chromatography, the situation is different because the Schmidt number in the liquid increases about 1000 times and the flow-rate has about one-tenth the value. The Reynolds number is about a factor of ten smaller, which helps to reduce R_F but not significantly. The similar correlation for R_F in liquid chromatography is[14]:

$$R_F = 0.139 \, R u^{-1} (\mathrm{Re}/\varepsilon)^{0.66} \mathrm{Sc}^{0.58} \tag{23}$$

With these approximate values, R_F is about 0.74, which is large enough to make the approximation in eqn. 21c of 21d questionable because the factor $\lambda_s K$ in liquid chromatography is likely to be higher than those in GC. A recent study by Kura[15] of acid hydrolysis of tetrametaphosphate in a liquid chromatograph indicated that the factor $\lambda_s K$ can be on the order of unity; therefore $R_F \lambda_s K$ also can be on the order of unity. The estimate given here cannot be used to draw a definite conclusion because the correlation equation was derived from data using particles with much larger size. It is prudent to point out the possible effect of interfacial mass transfer on the measurement of the rate constant. It is possible also to use a reactant to measure the value of the interfacial resistance, which is addressed in the next section.

Moment analysis

The Laplace transform of the gas-phase concentration can be inverted by the method of contour integration. Even for the simplest step-input concentration change, the result is an infinite series of improper integrals[10]. A more convenient way to determine the parameter is through the moment-analysis method. The nth moment for a peak is defined as

$$\mu_n = \int_0^\infty T t^n \, dt \tag{24}$$

where T is the transmission. The area ratio in eqn. 21 is simply the zeroth moment. The nth central moment, which is more useful for determining the parameters, is defined as:

$$\bar{\mu}_n = \int_0^\infty T(t - \mu_1)^n \, dt \tag{25}$$

The advantage of using moments is that one does not need to know the analytical expression for the output peak in order to relate the experimental results. To obtain this relationship, we first use the Laplace transform:

$$\mu_n = \lim_{p \to 0} \left[\frac{\left(-\dfrac{\partial}{\partial p}\right)^n \displaystyle\int_0^\infty e^{-pt} T \, dt}{\tilde{f}(p)} \right] \tag{26}$$

The central moment is given by:

$$\bar{\mu}_n = \sum_{k=0}^{n} \binom{n}{k} (-\mu_1)^k \, \mu_{n-k} \tag{27}$$

To proceed with the moment analysis, we assume that the input signal is a rectangular change with width, τ:

$$f(t) = C_0 \qquad 0 < t < \tau \tag{28a}$$

$$= 0 \qquad t > \tau \tag{28b}$$

The Laplace transform is:

$$\tilde{f}(p) = \frac{1 - e^{-\tau p}}{p} \cdot C_0 \tag{29}$$

The second-order central moment has the following relation[16]:

$$\left(\bar{\mu}_2 - \frac{\tau^2}{12} \right) \frac{u}{L} = \frac{A}{u^2} + B \tag{30}$$

$$A = \frac{2D_L \left[1 + 3K(1-\varepsilon)/\varepsilon \cdot \dfrac{(\sigma_0 \coth \sigma_0 - 1)}{\sigma_0^2 \, (1 + R_F \lambda_s K)^2} \right]^2}{\left[1 + \dfrac{4D_L}{u^2}\left(\lambda_g + \dfrac{1-\varepsilon}{\varepsilon} \cdot \dfrac{\lambda_s K}{1 + R_F \lambda_s K} \right) \right]^{3/2}} \tag{31}$$

$$B = \left(\frac{1-\varepsilon}{\varepsilon} \right) \cdot \frac{\left[18 R_F K^2 \left(\dfrac{\sigma_0 \coth \sigma_0 - 1}{\sigma_0^2} \right)^2 - \dfrac{3K}{\lambda_s}\left(\dfrac{2}{\sigma_0^2} - \dfrac{\coth \sigma_0}{\sigma_0} - \operatorname{cosech}^2 \sigma_0 \right)(1 + R_F \lambda_s K) \right]}{\left[1 + \dfrac{4D_L}{u^2}\left(\lambda_g + \dfrac{1-\varepsilon}{\varepsilon} \cdot \dfrac{\lambda_s K}{1 + R_F \lambda_s K} \right) \right]^{1/2} (1 + R_F \lambda_s K)^3} \tag{32}$$

Here σ_0 denotes the value of σ for $p = 0$. By measuring R_{in}/R_{out} and $\bar{\mu}_2$ at several flow-rates, it is possible to calculate A and B and six parameters: D_L, D_s, λ_s, λ_g, R_F

and K. It is noted that both A and B involve R_F, which is a function of flow-rate. One might argue that D_L is a function of flow-rate also. As long as the flow-rate does not vary too much (a factor of two is enough to apply eqn. 30), eqns. 22 and 23 indicate that R_F is a weak function of the flow-rate and can be assumed constant. In experimental work involving no chemical reaction, a linear plot of the second-order central moment[16] or the first order moment[17] of the transmission curve is usually observed, and it is safe to assume that the interfacial resistance is not important. When there is a chemical reaction, the factor R_F is no longer negligible as we mentioned in the previous section. Since eqn. 21 is not influenced by solid-phase diffusion, measurement of the transmission through a chromatographic column with a chemical reaction will be a sensitive method for studying interfacial mass-transfer resistance.

Glueckauf–Coates approximation

Glueckauf and Coates[18] pointed out that solid-phase diffusion (without a chemical reaction) can be approximated by the formula:

$$\frac{d\overset{\triangle}{q}}{dt} = k_s(kC - q) \tag{33}$$

This expression is much simpler than eqn. 2. Glueckauf and Coates indicated that the magnitude of k_s is of the order of D_s/R^2. Since analysts are generally interested in the output peak, we attempt to find out the best value of k_s such that:

$$\int_0^\infty [C_{true}(t) - C_{approx.}(t)] (t - \bar{t})^2 \, dt = 0 \tag{34a}$$

$$\int_0^\infty C_{true}(t) (t - \bar{t})^2 \, dt = \int_0^\infty C_{approx.}(t) (t - \bar{t})^2 dt \tag{34b}$$

This condition is equivalent to having the same $\bar{\mu}_2$. For the case of no reaction (*viz.*, $\lambda_s = \lambda_g = 0$), eqn. 34b becomes:

$$2\left(\frac{1 - \varepsilon}{\varepsilon}\right)K\left(KR_F + \frac{R^2}{15D_s}\right) = 2\left(\frac{1 - \varepsilon}{\varepsilon}\right) \cdot \frac{K}{k_s} \tag{35}$$

We can solve eqn. 35 for the best value of k_s:

$$k_s = \frac{1}{KR_F + (R^2/15D_s)} \tag{36}$$

It can be seen that the best value of k_s depends on the flow-rate, u, through R_F. In a recent paper[19], we used the Glueckauf and Coates approximation to derive the asymptotic concentration profile and to evaluate the coefficient k_s. The results show

an increase in the values of k_s at high flow-rates. This observation is in qualitative agreement with eqn. 35. Since an approximation method cannot give a universal coefficient for a system with either a linear isotherm or a non-linear isotherm, a new approach is needed.

SYMBOLS

C	Gas-phase concentration (moles/cm³)
C_0	Inlet concentration (moles/cm³)
D_L	Longitudinal diffusion coefficient (cm²/sec)
D_s	Solid-phase diffusion coefficient (cm²/sec)
K	Volume equilibrium constant
k_f	Mass transfer coefficient (cm/sec)
k_s	$1/R_F$ (sec⁻¹)
L	Length of chromatographic column (cm)
m	$\varepsilon/(1 - \varepsilon)$
p	Laplace transform variable (sec⁻¹)
$\overset{\triangle}{q}$	Solid-phase concentration (moles/cm³)
q	Average solid-phase concentration (moles/cm³)
q_s	Surface concentration (moles/cm³)
r	Internal radial coordinate (cm) inside particles
R	Radius (cm) of particles
R_F	$R/3k_f$; film resistance (sec)
R_{in}	Total amount of reactant at column inlet
R_{out}	Total amount of reactant at column outlet
Re	Reynolds number
Sc	Schmidt number
t	Time (sec)
T	$C(z,t)/C_0$ transmission
u	Linear flow velocity (cm/sec)
Y_A	Defined in eqn. 18
Y_D	Defined in eqn. 13
Y_T	Defined in eqn. 12
z	Longitudinal coordinate (cm)
ε	Void fraction of adsorber bed
λ_g	Gas-phase reaction-rate constant (sec⁻¹)
λ_s	Solid-phase reaction-rate constant (sec⁻¹)
μ_n	nth order moment
$\bar{\mu}_n$	nth order central moment
σ	$R\sqrt{(p + \lambda_s)/D_s}$
σ_0	$R\sqrt{\lambda_s/D_s}$
τ	Duration (sec) of pulse in gas-phase concentration

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