

Assumption of Local Equilibrium in Adsorption Processes

David C. Koopman, J. Vernon Cole, and Hong H. Lee
Dept. of Chemical Engineering, University of Florida, Gainesville, FL 32611

A local equilibrium between the concentration of adsorbate in the bulk fluid and surface phases is often assumed in the description of adsorption processes. This assumption leads to a considerable simplification in the problem by allowing an equilibrium treatment of the relationship between adsorbate concentration and surface coverage. The assumption indicates that the fractional coverage of the adsorbent by an adsorbate at any point in the process is in dynamic equilibrium with the adsorbate concentration in solution. Simple criteria developed here determine conditions under which such an assumption is justified.

The local equilibrium assumption has been used in an equilibrium theory of parametric pumping (Pigford et al., 1969) to develop a theory for multicomponent chromatography (Rhee et al., 1970), to analyze multicomponent ion exchange adsorption separations in packed beds (Helfferich, 1967), and to model the concentration profiles during impregnation of porous catalysts (Vincent and Merrill, 1974). The assumption is almost invariably invoked in temperature- and pressure-swing adsorption separation modeling (Yang, 1987). Often this takes the form of a Langmuir isotherm or a linear version of the isotherm.

Many of the empirical guidelines used in adsorption process engineering, such as that mass transfer is the rate-limiting step rather than adsorption kinetics, were developed from experience with processes involving adsorption of simple gas-phase molecules, strong adsorbents, and so on. Adsorption processing's scope has expanded considerably over the years, and adsorption separations have a significant foothold in the environmental and biochemical fields today. Engineers must deal with novel systems more often than in the past. Guidelines for good judgments are of great value in such an environment. In view of the importance of the above separation processes, as well as the significant role that adsorption plays in catalyst preparation (such as, Komiyama et al., 1980), an investigation of the conditions, under which such an assumption can be justified, is long overdue.

Adsorption Problem

Consider the competitive adsorption of n species from a

fluid onto a solid adsorbent in a packed bed. Species' concentrations evolve based on the response times associated with various resistances, such as dispersion in the bulk fluid, mass transfer to the surface, convection, diffusion in porous adsorbents, and kinetics. To establish a direct absolute criteria between adsorption kinetic rate effects and bulk fluid convection effects, assume that all effects of mass transfer are negligible. The ultimately derived criteria will consequently state only when adsorption kinetics cannot be considered in equilibrium relative to bulk fluid change rates. The relative importance of mass transfer rate effects to either bulk convection or adsorption kinetic rate effects will not be established by what follows. These assumptions yield the following solute mass balances:

Fluid phase:

$$\frac{\partial c_i}{\partial t} + v(t) \frac{\partial c_i}{\partial z} = -B_i \frac{\partial \theta_i}{\partial t}, \quad i = 1, 2, \dots, n \quad (1)$$

Solid phase:

$$\frac{\partial (q_{si} \theta_i)}{\partial t} = k_{ai} c_i \left[1 - \sum_{j=1}^n \theta_j \right] - k_{di} \theta_i \quad (2)$$

where c_i is the concentration of solute species i in the fluid, θ_i is the fractional coverage of the adsorbent surface by species i , v is the interstitial fluid velocity, q_{si} is the saturation surface concentration of adsorbate i in (moles adsorbate/weight adsorbent), k_{ai} is the adsorption rate constant, k_{di} is the desorption rate constant, and B is a physical constant given by

$$B_i = (1 - \epsilon) \rho_s q_{si} / \epsilon \quad (3)$$

where ϵ is the bed voidage and ρ_s is the solid density. The Langmuir isotherm was selected to represent competitive adsorption kinetics. These balance equations can be rendered dimensionless to yield:

$$\frac{\partial y_i}{\partial \tau} + u(\tau) \frac{\partial y_i}{\partial \gamma} = -\eta_i \frac{\partial \theta_i}{\partial \tau} \quad (4)$$

Correspondence concerning this work should be addressed to H. H. Lee.

$$\frac{\partial \theta_i}{\partial \tau} = \chi_i \left[y_i \left(1 - \sum_{j=1}^n \theta_j \right) - \theta_i / K_{Li} \right] \quad (5)$$

where

$$y_i = c_i / (c_{inlet})_i, \tau = t/t_r, u = vt_r/z, \gamma = z/Z \quad (6)$$

$$\chi_i = k_{ai} t_r (c_{inlet})_i / q_{si}, K_{Li} = k_{ai} (c_{inlet})_i / k_{di} \quad (7)$$

Here, $(c_{inlet})_i$ is the concentration of species i at the bed inlet, t_r is the time it takes for the fluid to reach the bed outlet, and Z is the bed length.

The local equilibrium assumption views the adsorption and desorption rates to be much faster than the rate at which the adsorbate concentration reaches its steady state. Therefore, an equilibrium is reached locally between θ and y in a short time span. Under this assumption, $\partial \theta_i / \partial \tau \approx 0$, and Eq. 5 simplifies to:

$$y_i \left(1 - \sum_{j=1}^n \theta_j \right) = \theta_i / K_{Li} \quad (8)$$

which, when solved for θ_i , yields the typical Langmuir isotherm for competitive adsorption as expected. This equation is then used in Eq. 4 for θ_i , transforming the equation to one in terms of y_i only, which results in considerable simplification of the model.

Conditions for Local Equilibrium

To examine the conditions under which the local equilibrium assumption can be made consider a single solute system for which Eq. 5 can be written as:

$$\frac{\partial \theta_1}{\partial \tau} = \chi_1 [y_1 (1 - \theta_1) - \theta_1 / K_{L1}] \quad (9)$$

If y_1 is relatively constant at \bar{y}_1 , that is, it reaches a pseudo-steady state much faster than θ , then Eq. 9 can be solved to obtain:

$$\theta_1 = \frac{\bar{y}_1}{\bar{y}_1 + 1/K_{L1}} [1 - e^{(-\chi_1(\bar{y}_1 + 1/K_{L1})\tau)}] \quad (10)$$

for $\theta_1 = 0$ at $\tau = 0$. For a conservative criterion given later, \bar{y}_1 will ultimately be set to zero, so considering y_1 approximately constant is not a serious constraint on the generality of the approach below. If sufficient time is allowed for equilibrium to be reached, the exponential term in Eq. 10 will vanish to give the familiar equilibrium relationship:

$$\theta_1 = \frac{K_{L1} \bar{y}_1}{1 + K_{L1} \bar{y}_1} \quad (11)$$

In most applications, the output of the system for $\tau \geq 1$ is of primary interest: the output of the system after the fluid stream entering the bed at time zero reaches the bed outlet. Therefore, it is sufficient to consider the magnitude of the argument of the exponential function without τ , $\chi_1(\bar{y}_1 + 1/K_{L1})$ to determine the rate at which local equilibrium is reached. Since $0 \leq \bar{y}_1 \leq 1$,

a conservative criterion is obtained if \bar{y}_1 is set to zero. Therefore, a condition for local equilibrium for a single solute system is:

$$\chi_1 / K_{L1} > A \quad (12)$$

where A is a constant to be selected. If a value of three is chosen for A , a maximum of 5% relative error between the equilibrium and exact value of θ_1 will result since $\exp(-3) \approx 0.05$; a value of four for A gives a maximum relative error less than 2%, and so on. In terms of the original parameters, Eq. 12 can be written as:

$$t_r k_{d1} / q_{s1} > A \quad (13)$$

It is seen that the local equilibrium assumption is more likely to be valid for larger residence times (lower throughputs), larger desorption rate constants, and smaller surface concentrations of active sites. A comparison between the correct solution and the solution based on the local equilibrium assumption is given in Figures 1 and 2 for a sludge solute system.

A criterion for the validity of the local equilibrium approximation for multicomponent systems can be obtained by a straightforward extension of the single solute case. As for the single solute system, Eq. 5 can be written for pseudo-constant $y_i = \bar{y}_i$ in the following matrix form:

$$\frac{\partial \underline{\theta}}{\partial \tau} = -\underline{G} \underline{\theta} + \underline{H} \underline{\bar{y}} \quad (14)$$

where $\underline{\theta}^T = [\theta_1, \theta_2, \dots, \theta_n]$, $\underline{\bar{y}} = [\bar{y}_1, \bar{y}_2, \dots, \bar{y}_n]$, and \underline{G} is a matrix in which the diagonal elements are $\chi_i(\bar{y}_i + 1/K_{Li})$ and all other elements of the i th row are $\chi_i \bar{y}_j$. \underline{H} is a diagonal matrix with H_{ii} given by χ_i . The solution of Eq. 14 is a finite expansion in exponential functions of $-\lambda_i \tau$, where the λ_i are eigenvalues of \underline{G} . The smallest Eigenvalue of the matrix \underline{G} determines the speed at which the local equilibrium is reached.

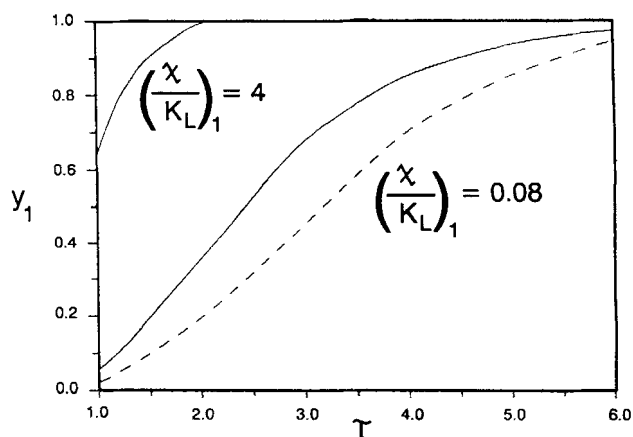


Figure 1. Normalized concentration, y_1 , at the packed bed exit as a function of the scaled time, τ , and the dimensionless group, χ_i/K_{Li} .

—, solution of exact equations; ----, solution using the local equilibrium assumption.

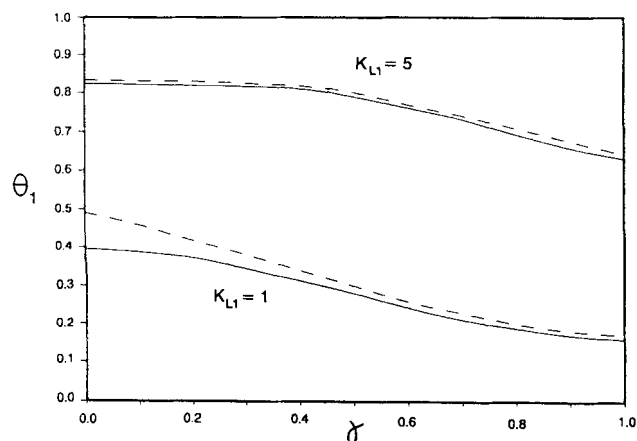


Figure 2. Fractional coverage of adsorbent, θ_1 , as a function of normalized reactor length at the time, $\tau = 1^+$, for $\chi_i/K_{Li} = 0.8$.

—, solution of exact equations; ----, solution using the local equilibrium assumption.

To obtain a simple criterion it is not necessary to solve Eq. 14. The eigenvalues of \underline{G} can be bound by examining the equation $\underline{G}\theta = \lambda\theta$. An implicit solution for λ_i in terms of θ_i can be obtained directly:

$$\lambda_i = \chi_i/K_{Li} + (\chi_i \bar{y}_i / \theta_i) \sum_{j=1}^n \theta_j \quad (15)$$

Equation 15 is obtained by carrying out the matrix multiplications in index form and solving for λ_i , remembering that trivial solutions, $\theta = 0$, are not desired. On purely physical grounds, all of the eigenvalues must be positive based on this expression. To devise a conservative criterion, it is sufficient to find a term that is smaller than all of the λ_i . Since the second term in the sum in Eq. 15 is always nonnegative, it follows that $\lambda_i \geq \chi_i/K_{Li}$. Therefore, the minimum element in the set $\{\chi_i/K_{Li}\}$, $(\chi_i/K_{Li})_{\min}$, will be as small as or smaller than all the eigenvalues of \underline{G} . Then, by analogy with Eqs. 12 and 13 a criterion based on this term is:

$$(\chi_i/K_{Li})_{\min} = (t_r k_{di}/q_{si})_{\min} > A \quad (16)$$

where the subscript, min, denotes the smallest of the approximate eigenvalues. The value of A is chosen in the same manner as for the single solute case, for example, a value of 3 gives a maximum error of 5%. If $\theta_{i,\min}$ is negligible and $\bar{y}_{i,\min}$ is nonzero, then by Eq. 15, the criterion could be quite conservative.

According to the criterion of Eq. 16, only the smallest value of χ_i/K_{Li} needs to be considered to determine the validity of the local equilibrium assumption for a multicomponent system.

If, however, the component having the smallest eigenvalue is present in trace amounts, the next smallest approximate eigenvalue may be checked. Likewise, if there is one component of main interest, the approximate eigenvalue of only that component may be considered. Furthermore, it should be noted that all of the quantities in the criteria are either known (t_r) or measurable (k_d and q_s).

Notation

- A = arbitrary constant associated with relative error in Eqs. 12 and 16
- B = quantity defined by Eq. 3
- c_i = solute concentration of species i in the fluid phase
- $(c_{\text{inlet}})_i$ = c_i at the bed inlet
- \underline{G} = matrix in Eq. 14
- k_{ai} = adsorption rate constant for species i
- k_{di} = desorption rate constant for species i
- K_{Li} = quantity defined in Eq. 7
- q_{si} = saturation surface concentration of species i in moles i /weight solid
- t = time
- t_r = time for the fluid to travel the length of the bed
- u = normalized velocity defined in Eq. 6
- v = interstitial fluid velocity
- y_i = $c_i/(c_{\text{inlet}})_i$
- \bar{y}_i = pseudo-constant value of y_i
- \bar{y} = vector consisting of \bar{y}_i
- z = bed length coordinate
- Z = bed length

Greek letters

- γ = z/Z
- ϵ = bed voidage
- θ_i = fractional coverage of adsorption sites by solute i
- $\underline{\theta}$ = vector consisting of θ_i
- λ_i = eigenvalues of the matrix \underline{G}
- ρ_s = solid (adsorbent) density
- τ = t/t_r
- χ_i = characteristic group defined in Eq. 7

Literature Cited

- Helfferich, F., "Multicomponent Ion Exchange in Fixed Beds," *Ind. Eng. Chem. Fund.*, **6**, 362 (1967).
- Komiyama, M., R. P. Merrill, and H. F. Harnsberger, "Concentration Profiles in Impregnation of Porous Catalysts: Nickel on Alumina," *J. Catal.*, **63**, 35 (1980).
- Pigford, R. L., B. Baker, and D. E. Blum, "An Equilibrium Theory of the Parametric Pump," *Ind. Eng. Chem. Fund.*, **8**, 144 (1969).
- Rhee, H. K., R. Aris, and N. R. Amundson, "On the Theory of Multicomponent Chromatography," *Phil. Trans. Roy. Soc. Lond. A.*, **267**, 419 (1970).
- Vincent, R. C., and R. P. Merrill, "Concentration Profiles of Solute in Impregnation of Porous Catalysts," *J. Catal.*, **35**, 206 (1974).
- Yang, R. T., *Gas Separation by Adsorption Processes*, Butterworth, Boston (1987).

Manuscript received Dec. 27, 1991.