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Frequency Response of Continuous-Flow Adsorber for Multicomponent System

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Abstract−In this paper, we present a theoretical analysis of the frequency response of a continuous-flow adsorber with periodic modulation of the inlet flow-rate to measure multicomponent diffusion kinetics in porous media. Micropore diffusion kinetics is assumed for the intraparticle mass transfer mechanism and three different shapes of microparticle are considered: slab, cylinder, and sphere. Simulation results for a binary system show that the frequency response of the faster diffusing component is strongly influenced by the slower component. The out-of-phase characteristic function of the frequency response of the faster diffusing component shows maximum and minimum points. The deviation between these maximum and minimum values becomes smaller when the cross-terms of diffusivity go to zero, while the deviation becomes larger when the cross-terms of the adsorption equilibrium constant go to zero. Contrary to the behaviour of the out-of-phase function of the faster diffusing component, the out-of-phase function of the slower diffusing component shows no extrema at all. The in-phase characteristic function of the frequency response of the continuous-flow adsorber is not affected by the overflow parameter.

Key words: Multicomponent Diffusion, Frequency Response, Continuous-Flow Adsorber

INTRODUCTION

Because of its importance in the study of catalytic or noncatalytic gas-solid reactions, the problem of gaseous diffusion kinetics in porous media has attracted much attention in the literature. As a result, a variety of methods for investigation of the kinetics have been presented. The mass transport phenomena in porous media include contributions from bulk, Knudsen and pore diffusion, and viscous flow, which are further complicated by interactions with adsorption and surface diffusion on the internal surface of the porous media. In order to determine reliably the contribution of each transport mechanism and the relevant parameters, some experimental techniques are needed. To achieve this goal, one of the following techniques can be used: gas chromatography, diffusion cell, gravimetric method using a microbalance, zero length column, and differential adsorption bed. The advantages and disadvantages of these techniques are reported in the literature [Park et al., 1996].

Recently, a frequency response (FR) method was developed, for the investigation of the diffusion and adsorption kinetics in porous media [Jordi and Do, 1992, 1993, 1994; Park et al., 1998a, b; Petkovska and Do, 1998; Sun et al., 1993, 1994; Sun and Bourdin, 1993; Sun and Do, 1995, 1996; Yasuda and Saeki, 1978; Yasuda, 1982; Yasuda and Sugawara, 1984]. The potential of this method was extended to systems with chemical reactions [Yasuda, 1989; 1993; Yasuda et al., 1995]. In the FR method the frequency response is usually investigated in a batch system in which the gas pressure or concentration is changed by a forced periodic modulation of the reservoir volume, although FR in continuous flow systems with periodic modulation of the inlet gas concentration [Ngai and Gomes, 1996] or the inlet molar flow rate [Park et al., 1998a, b]. The main advantages of FR using modulation of the inlet flow-rate over the conventional FR using modulation of the reservoir volume are the following [Park et al., 1998a, b]:

- High frequencies of the inlet molar flow-rate modulations are easy to obtain in practice, contrary to volume modulations.
- Large relative amplitudes of the inlet flow-rate can be used.

The analysis of the multicomponent diffusion in a porous media requires knowledge of both the main-terms and cross-terms of diffusivity. However, our understanding of multicomponent diffusion is very limited [Qureshi and Wei, 1990; Markovska et al., 1999], and a very limited number of papers for the FR of multicomponent diffusion are available [Yasuda and Matsumoto, 1989; Sun et al., 1994].

The objective of this paper is to present a theoretical analysis of the frequency response of a continuous-flow adsorber with periodic modulation of the inlet flow-rate for the multicomponent diffusion in porous media. Micropore diffusion kinetics is assumed for the intraparticle mass transfer mechanism and three different shapes of microparticle are considered: slab, cylinder, and sphere.

PROBLEM FORMATION AND MATHEMATICAL MODEL

Consider a continuous-stirred gas reservoir, in which a known amount of porous particles is loaded. The particles are assumed to be of uniform size. At time t=0, a stream of an ideal gas mixture of n components is introduced to the reservoir with periodic flow rate and at the same time a flowing stream out of the reservoir is started. We assume that the system is isothermal, and that the diffusion parameters are constant.

The mass balance describing the concentration distribution inside

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a porous particle for the micropore diffusion kinetics [Park et al., 1998a] is:

$$\frac{\partial \mathbf{C}_\mu}{\partial t}=[D]\frac{1}{r^\sigma}\frac{\partial}{\partial r}\left(r^\sigma\frac{\partial \mathbf{C}_\mu}{\partial r}\right) \tag{1}$$

where $\mathbf{C}_\mu$ is a vector of dimension n denoting the concentration in the micropore within particles and [D] is a square matrix of diffusivities in which the off-diagonal terms are generally non-zero; r is the coordinate variable of microparticles within a particle, and σ is a geometric factor of the particle (0 for slab, 1 for cylinder and 2 for sphere). The initial and boundary conditions are

$$\text{at } t=0 \qquad \mathbf{C}_\mu=\mathbf{0} \tag{2}$$

$$\text{at } r=0, \qquad \frac{\partial \mathbf{C}_\mu}{\partial r}=\mathbf{0} \tag{3}$$

$$\text{at } r=R_\mu \qquad \mathbf{C}_\mu=[K]\mathbf{C} \tag{4}$$

where $\mathbf{C}$ is the vector of dimension n denoting the concentration in the reservoir and [K] is a square matrix of adsorption equilibrium constant. The mass balance around the whole reservoir is

$$\frac{d\mathbf{C}}{dt}+\beta\frac{d<\mathbf{C}_\mu>}{dt}=\alpha X(t)\mathbf{y}-\gamma\mathbf{C} \tag{5a}$$

$$<\mathbf{C}_\mu>=\frac{\sigma+1}{R_\mu^{\sigma+1}}\int_0^{R_\mu} r^\sigma \mathbf{C}_\mu dr \tag{5b}$$

where $\mathbf{y}$ is the vector of dimension *n* denoting the mole fraction in the inlet stream and α is the intensity parameter measuring the magnitude of the molar supply into the reservoir, β is the capacity parameter, and γ is the overflow parameter, which are given as follows:

$$\alpha=\frac{N}{V};\quad \beta=\frac{V_\mu}{V};\quad \gamma=\frac{q}{V}$$

X(t) in Eq. (5) is the forcing function, which defines the form of the periodic modulation of the inlet flow rate. We use the sinusoidal wave function:

$$X(t)=1+\nu\sin\omega t \tag{6}$$

The initial condition for Eq. (5) is

$$\text{at } t=0 \qquad \mathbf{C}=\mathbf{0} \tag{7}$$

SOLUTION OF THE MODEL EQUATIONS

The frequency response of the above model can be analytically obtained by using matrix manipulation. The key point is to diagonalize the diffusivity matrix [D] in terms of the eigenvalues and eigenvectors. With the diagonalization of the diffusivity matrix, the n coupled diffusion equations [Eq. (1)] can be decoupled into n individual equations, which can be easily solved as in the case of pure component systems by using the Laplace transform, since the model is linear.

1. Diagonalization of Diffusivity Matrix

First we diagonalize the diffusivity matrix:

$$[Z]^{-1}[D][Z]=[\Lambda] \tag{8}$$

where [Λ] and [Z] are the eigenvalue matrix and the eigenvector matrix, respectively. For a binary system, [Λ] and [Z] are:

$$[\Lambda]=\begin{bmatrix}\lambda_1 & 0\\ 0 & \lambda_2\end{bmatrix};\quad [Z]=\begin{bmatrix}Z_{11} & Z_{12}\\ Z_{21} & Z_{22}\end{bmatrix} \tag{9}$$

Then we can obtain for the binary system:

$$\lambda_{1,2}=\frac{1}{2}[D_{11}+D_{22}\pm\sqrt{(D_{11}-D_{22})^2+4D_{12}D_{21}}] \tag{10}$$

$$[Z]=\begin{bmatrix}1 & \dfrac{D_{12}}{\lambda_2-D_{11}}\\ \dfrac{D_{21}}{\lambda_1-D_{22}} & 1\end{bmatrix}=\begin{bmatrix}1 & \dfrac{-D_{12}}{\delta}\\ \dfrac{D_{21}}{\delta} & 1\end{bmatrix} \tag{11}$$

$$[Z]^{-1}=\frac{1}{1+\dfrac{D_{12}D_{21}}{\delta^2}}\begin{bmatrix}1 & \dfrac{D_{12}}{\delta}\\ \dfrac{-D_{21}}{\delta} & 1\end{bmatrix} \tag{12}$$

$$\delta=\lambda_1-D_{22}=-(\lambda_2-D_{11}) \tag{13}$$

2. Decoupling of Diffusion Equation

In order to decouple Eq. (1) we introduce vector $\mathbf{u}$, such that

$$\mathbf{C}_\mu=[Z]\mathbf{u} \tag{14}$$

Then Eq. (1) can be decoupled as

$$\frac{\partial u_k}{\partial t}=\lambda_k\frac{1}{r^\sigma}\frac{\partial}{\partial r}\left(r^\sigma\frac{\partial u_k}{\partial r}\right) \tag{15}$$

$$(k=1, 2, \Lambda, n)$$

The initial and boundary conditions become

$$\text{at } t=0 \qquad u_k=0 \tag{16}$$

$$\text{at } r=0, \qquad \frac{\partial u_k}{\partial r}=0 \tag{17}$$

$$\text{at } r=R_\mu \qquad \mathbf{u}=[Z]^{-1}[K]\mathbf{C} \tag{18}$$

3. Transfer Function, Q(s)

Now the solution in Laplace domain of Eq. (14) can be obtained as:

$$\overline{\mathbf{C}}_\mu=[Z]\overline{\mathbf{u}} \tag{19}$$

where

$$\overline{\mathbf{u}}=\text{diag}\left[\frac{f_k(r,s)}{f_k(R_\mu,s)}\right][Z]^{-1}[K]\overline{\mathbf{C}} \tag{20}$$

The function f(r, s) in Eq. (20) is given by:

$$f_k(r,s)=\begin{cases}\cosh\left(r\sqrt{\dfrac{s}{\lambda_k}}\right) & \text{for } \sigma=0\\ I_0\left(r\sqrt{\dfrac{s}{\lambda_k}}\right) & \sigma=1\\ \dfrac{1}{r}\sinh\left(r\sqrt{\dfrac{s}{\lambda_k}}\right) & \text{for } \sigma=2\end{cases} \tag{21}$$

From Eq. (20) the volumetric average for $\overline{\mathbf{C}}_\mu$ can be obtained as:

$$<\overline{\mathbf{C}}_\mu> = [T]\overline{\mathbf{C}} \tag{22}$$

where

$$[T]=[Z]\mathrm{diag}(F_k(s))[Z]^{-1}[K] \tag{23}$$

The function F(s) is defined by:

$$F_k(s) = \frac{\tanh\left(R_\mu\sqrt{\frac{s}{\lambda_k}}\right)}{R_\mu\sqrt{\frac{s}{\lambda_k}}} \quad \text{for } \sigma = 0 \tag{24a}$$

$$F_k(s) = 2\left(\frac{1}{R_\mu\sqrt{\frac{s}{\lambda_k}}}\right)\left[\frac{I_1\left(R_\mu\sqrt{\frac{s}{\lambda_k}}\right)}{I_0\left(R_\mu\sqrt{\frac{s}{\lambda_k}}\right)}\right] \quad \text{for } \sigma = 1 \tag{24b}$$

$$F_k(s) = 3\left(\frac{R_\mu\sqrt{\frac{s}{\lambda_k}}\coth\left(R_\mu\sqrt{\frac{s}{\lambda_k}}\right)-1}{\left(R_\mu\sqrt{\frac{s}{\lambda_k}}\right)^2}\right) \quad \text{for } \sigma = 2 \tag{24c}$$

Eq. (22) can be rearranged to obtain the transfer function for the particle:

$$<\overline{\mathbf{C}}_\mu> = \mathrm{diag}(Q_k(s))\overline{\mathbf{C}} \tag{25}$$

where the element Q_k of the diagonal matrix $\mathrm{diag}(Q_k(s))$ can be obtained as:

$$Q_k(s) = \sum_{i=1}^{n} T_{ki}\left(\frac{\overline{C}_i}{\overline{C}_k}\right) \tag{26}$$

The expression for $\overline{C}_i/\overline{C}_k$ will be given in the next section [see Eq. (32)]. As shown by Eq. (25), The transfer function $Q_k(s)$ relates the bulk concentration in the gas phase to the mean concentration in the adsorbed phase. We note that when all the cross-term elements of matrices [D] are zero, $Q_k(s)$ reduces to the function $F_k(s)$. Note that the function $F_k(s)$ is the particle transfer function in case of pure component systems [Park et al., 1998b].

4. Overall Transfer Function for Adsorber, G(s)

The Laplace transform of Eq. (5) is:

$$s(\overline{\mathbf{C}} + \beta<\overline{\mathbf{C}}_\mu>) = \alpha\overline{X}\mathbf{y} - \gamma\overline{\mathbf{C}} \tag{27}$$

Substituting Eq. (25) for $<\overline{\mathbf{C}}_\mu>$, we have

$$s\left(1+\frac{\gamma}{s}\right)\left([I] + \frac{\beta}{1+\gamma/s}\mathrm{diag}(Q_k(s))\right)\overline{\mathbf{C}} = \alpha\overline{X}\mathbf{y} \tag{28}$$

Thus, the overall transfer function for the kth component can be obtained as

$$G_k(s) \equiv \frac{\overline{C}_k}{\alpha y_k\overline{X}} = \frac{1}{s[1+\gamma/s+\beta Q_k(s)]} \tag{29}$$

To determine $\overline{C}_j/\overline{C}_k$ in Eq. (26), we rearrange Eq. (27) after substituting Eq. (22) for $<\overline{\mathbf{C}}_\mu>$ as follows:

$$s\left(1+\frac{\gamma}{s}\right)\left([I] + \frac{\beta}{1+\gamma/s}[T]\right)\overline{\mathbf{C}} = \alpha\overline{X}\mathbf{y}; \quad s\left(1+\frac{\gamma}{s}\right)\overline{\mathbf{C}} = \alpha\overline{X}[B]\mathbf{y} \tag{30}$$

where square matrix [B] is defined by

$$[B]^{-1} = [I] + \frac{\beta}{1+\gamma/s}[T] \tag{31}$$

Then we can obtain

$$\frac{\overline{C}_i}{\overline{C}_k} = \sum_{j=1}^{n} B_{ij}y_j \Big/ \sum_{j=1}^{n} B_{kj}y_j \tag{32}$$

Substituting Eq. (32) into Eq. (26), we obtain the exact expression

Table 1. Transfer function Q(s) for binary systems

$$Q_1(s) = T_{11}(s) + T_{12}(s)\frac{y_1B_{21}+y_2B_{22}}{y_1B_{11}+y_2B_{12}} \equiv T_{11}(s) + T_{12}(s)R_{21}(s) \tag{34a}$$

$$Q_2(s) = T_{21}(s)\frac{y_1B_{11}+y_2B_{12}}{y_1B_{21}+y_2B_{22}} + T_{22}(s) \equiv T_{21}(s)R_{12}(s) + T_{22}(s) \tag{34b}$$

$$T_{11}(s) = \frac{1}{1+\frac{D_{12}D_{21}}{\delta^2}}\left[\left(K_{11}+\frac{D_{12}K_{21}}{\delta}\right)F_1(s) + \left(\frac{D_{12}D_{21}}{\delta^2}K_{11} - \frac{D_{12}K_{21}}{\delta}\right)F_2(s)\right] \tag{34c}$$

$$T_{12}(s) = \frac{1}{1+\frac{D_{12}D_{21}}{\delta^2}}\left[\left(K_{12}+\frac{D_{12}K_{22}}{\delta}\right)F_1(s) + \left(\frac{D_{12}D_{21}}{\delta^2}K_{12} - \frac{D_{12}K_{22}}{\delta}\right)F_2(s)\right] \tag{34d}$$

$$T_{21}(s) = \frac{1}{1+\frac{D_{12}D_{21}}{\delta^2}}\left[\left(K_{21}-\frac{D_{21}K_{11}}{\delta}\right)F_2(s) + \left(\frac{D_{12}D_{21}}{\delta^2}K_{21} + \frac{D_{21}K_{11}}{\delta}\right)F_1(s)\right] \tag{34e}$$

$$T_{22}(s) = \frac{1}{1+\frac{D_{12}D_{21}}{\delta^2}}\left[\left(K_{22}-\frac{D_{21}K_{12}}{\delta}\right)F_2(s) + \left(\frac{D_{12}D_{21}}{\delta^2}K_{22} + \frac{D_{21}K_{12}}{\delta}\right)F_1(s)\right] \tag{34f}$$

$$B_{11}(s) = \frac{1}{B_0(s)}(1+T_{22}(s)) \tag{34g}$$

$$B_{12}(s) = \frac{1}{B_0(s)}(-T_{12}(s)) \tag{34h}$$

$$B_{21}(s) = \frac{1}{B_0(s)}(-T_{21}(s)) \tag{34i}$$

$$B_{11}(s) = \frac{1}{B_0(s)}(1+T_{11}(s)) \tag{34j}$$

where

$$B_0(s) = 1 + \frac{\beta}{1+\gamma/s}T_{11}(s) + \frac{\beta}{1+\gamma/s}T_{22}(s) + \left(\frac{\beta}{1+\gamma/s}\right)^2 T_{11}(s)T_{22}(s) - \left(\frac{\beta}{1+\gamma/s}\right)^2 T_{11}(s)T_{21}(s) \tag{34k}$$

of $Q_k(s)$:

$$Q_k(s)=\sum_{i=1}^{n}\left(T_{ki}\sum_{j=1}^{n}B_{ij}y_j\Big/\sum_{j=1}^{n}B_{kj}y_j\right) \tag{33}$$

The transfer functions $Q_k(s)$ for binary systems are given in Table 1.

The overall transfer function G(s) relates the forcing function to the gas phase concentration in the reservoir. The difference between the semibatch adsorber (γ=0) and the conventional batch adsorber can be illustrated if the transfer function G(s) in Eq. (31a) is rearranged and put in a product of two functions as follows [Park et al., 1998a]:

$$G_k(s)=G_I(s)\cdot G_{II,k}(s) \tag{35}$$

where $G_I(s)$ and $G_{II,k}(s)$ are defined by

$$G_I(s)=\frac{1}{s} \tag{36}$$

$$G_{II,k}(s)=\frac{1}{1+\gamma/s+\beta Q_k(s)} \tag{37}$$

The first function $G_I(s)$ is simply the transfer function of a physical filling reservoir, defining the relation between the inlet flow rate $\alpha y_k\overline{X}$ and a hypothetical adsorbate concentration in the reservoir in the Laplace domain which would be obtained if no adsorbent and no outlet flow were present. The second function $G_{II,k}(s)$ defines in which way this adsorbate is distributed between the gas phase and the outlet flow. When no outlet flow was present (i.e., when γ=0), the second function $G_{II,k}(s)$ reduces to the transfer function of the conventional batch adsorber containing adsorbent [Park et al., 1998b].

CHARACTERISTIC FUNCTIONS OF FREQUENCY RESPONSE

The in-phase and out-of-phase characteristic functions for the element $F_k(s)$ can be defined as:

$$\delta_{R,k}-i\delta_{I,k}=\lim_{s\to i\omega}F_k(s) \tag{38}$$

Then, we can obtain:

For σ=0:

$$\delta_{R,k}=\frac{\sinh\left(R_\mu\sqrt{\frac{2\omega}{\lambda_k}}\right)+\sin\left(R_\mu\sqrt{\frac{2\omega}{\lambda_k}}\right)}{\left(R_\mu\sqrt{\frac{2\omega}{\lambda_k}}\right)\left[\cosh\left(R_\mu\sqrt{\frac{2\omega}{\lambda_k}}\right)+\cos\left(R_\mu\sqrt{\frac{2\omega}{\lambda_k}}\right)\right]}$$

$$\delta_{I,k}=\frac{\sinh\left(R_\mu\sqrt{\frac{2\omega}{\lambda_k}}\right)-\sin\left(R_\mu\sqrt{\frac{2\omega}{\lambda_k}}\right)}{\left(R_\mu\sqrt{\frac{2\omega}{\lambda_k}}\right)\left[\cosh\left(R_\mu\sqrt{\frac{2\omega}{\lambda_k}}\right)+\cos\left(R_\mu\sqrt{\frac{2\omega}{\lambda_k}}\right)\right]} \tag{39a}$$

For σ=1:

$$\delta_{R,k}=2\mathrm{Re}\left\{\frac{1}{R_\mu\sqrt{\frac{i\omega}{\lambda_k}}}\frac{I_1\left(R_\mu\sqrt{\frac{i\omega}{\lambda_k}}\right)}{I_0\left(R_\mu\sqrt{\frac{i\omega}{\lambda_k}}\right)}\right\}$$

$$\delta_{I,k}=2\mathrm{Im}\left\{\frac{-1}{R_\mu\sqrt{\frac{i\omega}{\lambda_k}}}\frac{I_1\left(R_\mu\sqrt{\frac{i\omega}{\lambda_k}}\right)}{I_0\left(R_\mu\sqrt{\frac{i\omega}{\lambda_k}}\right)}\right\} \tag{39b}$$

For σ=2:

$$\delta_{R,k}=3\left\{\frac{\sinh\left(R_\mu\sqrt{\frac{2\omega}{\lambda_k}}\right)-\sin\left(R_\mu\sqrt{\frac{2\omega}{\lambda_k}}\right)}{\left(R_\mu\sqrt{\frac{2\omega}{\lambda_k}}\right)\left[\cosh\left(R_\mu\sqrt{\frac{2\omega}{\lambda_k}}\right)-\cos\left(R_\mu\sqrt{\frac{2\omega}{\lambda_k}}\right)\right]}\right\}$$

$$\delta_{I,k}=3\left\{\frac{\sinh\left(R_\mu\sqrt{\frac{2\omega}{\lambda_k}}\right)+\sin\left(R_\mu\sqrt{\frac{2\omega}{\lambda_k}}\right)}{\left(R_\mu\sqrt{\frac{2\omega}{\lambda_k}}\right)\left[\cosh\left(R_\mu\sqrt{\frac{2\omega}{\lambda_k}}\right)-\cos\left(R_\mu\sqrt{\frac{2\omega}{\lambda_k}}\right)\right]}-\frac{2}{\left(R_\mu\sqrt{\frac{2\omega}{\lambda_k}}\right)^2}\right\} \tag{39c}$$

Now the overall in-phase and out-of-phase characteristic functions for the adsorber are defined as:

$$\frac{\eta_{R,k}}{\beta}=\mathrm{Re}\left\{\lim_{s\to i\omega}\left[Q_k(s)+\frac{\gamma}{\beta s}\right]\right\} \tag{40a}$$

$$\frac{\eta_{I,k}}{\beta}=-\mathrm{Im}\left\{\lim_{s\to i\omega}\left[Q_k(s)+\frac{\gamma}{\beta s}\right]\right\} \tag{40b}$$

The overall characteristic functions for binary systems are given in Table 2.

SIMULATION OF THE FREQUENCY RESPONSE

The data of Chen and Yang [1992] for the surface diffusion of CO_2 and C_2H_6 in 4A zeolite were used to simulate the characteristic function of the frequency response. These data are also used in Sun et al. [1994] to simulate their model. Values of parameters of this system are summarized below:

σ=2 (spherical microparticle);

$V=10^{-4}\ m^3$ $V_\mu=3\times10^{-7}\ m^3$

$R_\mu=1.7\times10^{-6}\ m$ $y_1=0.33$

$$T=298\ K\ [K]=\begin{bmatrix}0.38 & -0.13\\ -0.083 & 0.099\end{bmatrix}$$

$$[D]=\begin{bmatrix}1.4\times10^{-14} & 1.1\times10^{-14}\\ 3.7\times10^{-17} & 1.2\times10^{-16}\end{bmatrix}$$

Fig. 1 shows the in-phase and out-of-phase characteristic functions of the frequency response for the binary mixture of CO_2 and C_2H_6 in 4A zeolite when the outlet stream of the adsorber is closed (i.e., when γ=0). On the whole, similar observations to those of Sun et al. [1994] are shown in this figure: (1) The faster diffusing component (CO_2) is strongly influenced by the slower component. (2) The out-of-phase function of CO_2 is negative near the resonance frequency of C_2H_6. (3) The in-phase function has an overshoot near

Table 2. Overall characteristic functions of frequency response for binary systems

$$\frac{\eta_{R,1}}{\beta} = T_{R,11} + (T_{R,12}R_{R,21} - T_{I,12}R_{I,21}) \tag{41a}$$

$$\frac{\eta_{I,1}}{\beta} = T_{I,11} + (T_{R,12}R_{I,21} + T_{I,12}R_{R,21}) + \frac{\gamma}{\beta\omega} \tag{41b}$$

$$\frac{\eta_{R,2}}{\beta} = T_{R,22} + (T_{R,21}R_{R,12} - T_{I,21}R_{I,12}) \tag{41c}$$

$$\frac{\eta_{I,2}}{\beta} = T_{I,22} + (T_{R,21}R_{I,12} + T_{I,21}R_{R,12}) + \frac{\gamma}{\beta\omega} \tag{41d}$$

$$T_{R,11} = \frac{1}{1+\frac{D_{12}D_{21}}{\delta^2}}\left[\left(K_{11}+\frac{D_{12}K_{21}}{\delta}\right)\delta_{R,1} + \left(\frac{D_{12}D_{21}}{\delta^2}K_{11} - \frac{D_{12}K_{21}}{\delta}\right)\delta_{R,2}\right] \tag{41e}$$

$$T_{I,11} = \frac{1}{1+\frac{D_{12}D_{21}}{\delta^2}}\left[\left(K_{11}+\frac{D_{12}K_{21}}{\delta}\right)\delta_{I,1} + \left(\frac{D_{12}D_{21}}{\delta^2}K_{11} - \frac{D_{12}K_{21}}{\delta}\right)\delta_{I,2}\right] \tag{41f}$$

$$T_{R,12} = \frac{1}{1+\frac{D_{12}D_{21}}{\delta^2}}\left[\left(K_{12}+\frac{D_{12}K_{22}}{\delta}\right)\delta_{R,1} + \left(\frac{D_{12}D_{21}}{\delta^2}K_{12} - \frac{D_{12}K_{22}}{\delta}\right)\delta_{R,2}\right] \tag{41g}$$

$$T_{I,12} = \frac{1}{1+\frac{D_{12}D_{21}}{\delta^2}}\left[\left(K_{12}+\frac{D_{12}K_{22}}{\delta}\right)\delta_{I,1} + \left(\frac{D_{12}D_{21}}{\delta^2}K_{12} - \frac{D_{12}K_{22}}{\delta}\right)\delta_{I,2}\right] \tag{41h}$$

$$T_{R,21} = \frac{1}{1+\frac{D_{12}D_{21}}{\delta^2}}\left[\left(K_{21}-\frac{D_{21}K_{11}}{\delta}\right)\delta_{R,2} + \left(\frac{D_{12}D_{21}}{\delta^2}K_{21} + \frac{D_{21}K_{11}}{\delta}\right)\delta_{R,1}\right] \tag{41i}$$

$$T_{I,21} = \frac{1}{1+\frac{D_{12}D_{21}}{\delta^2}}\left[\left(K_{21}-\frac{D_{21}K_{11}}{\delta}\right)\delta_{I,2} + \left(\frac{D_{12}D_{21}}{\delta^2}K_{21} + \frac{D_{21}K_{11}}{\delta}\right)\delta_{I,1}\right] \tag{41j}$$

$$T_{R,22} = \frac{1}{1+\frac{D_{12}D_{21}}{\delta^2}}\left[\left(K_{22}-\frac{D_{21}K_{12}}{\delta}\right)\delta_{R,2} + \left(\frac{D_{12}D_{21}}{\delta^2}K_{22} + \frac{D_{21}K_{12}}{\delta}\right)\delta_{R,1}\right] \tag{41k}$$

$$T_{I,22} = \frac{1}{1+\frac{D_{12}D_{21}}{\delta^2}}\left[\left(K_{22}-\frac{D_{21}K_{12}}{\delta}\right)\delta_{I,2} + \left(\frac{D_{12}D_{21}}{\delta^2}K_{22} + \frac{D_{21}K_{12}}{\delta}\right)\delta_{I,1}\right] \tag{41l}$$

$$R_{R,12} = \frac{[y_1+\beta(y_1T_{R,22}-y_2T_{R,12})\mathbf{I}y_2+\beta(y_2T_{R,11}-y_1T_{R,21})] + \beta^2\left(y_1T_{I,22}-y_2T_{I,12}+\frac{\gamma}{\beta\omega}\right)\left(y_2T_{I,11}-y_1T_{I,21}+\frac{\gamma}{\beta\omega}\right)}{[y_2+\beta(y_2T_{R,11}-y_1T_{R,21})]^2 + \beta^2\left(y_2T_{I,11}-y_1T_{I,21}+\frac{\gamma}{\beta\omega}\right)^2} \tag{41m}$$

$$R_{I,12} = \frac{\beta[y_2+\beta(y_2T_{R,11}-y_1T_{R,21})]\left(y_1T_{I,22}-y_2T_{I,12}+\frac{\gamma}{\beta\omega}\right) - \beta[y_1+\beta(y_1T_{R,22}-y_2T_{R,12})]\left(y_2T_{I,11}-y_1T_{I,21}+\frac{\gamma}{\beta\omega}\right)}{[y_2+\beta(y_2T_{R,11}-y_1T_{R,21})]^2 + \beta^2\left(y_2T_{I,11}-y_1T_{I,21}+\frac{\gamma}{\beta\omega}\right)^2} \tag{41n}$$

$$R_{R,21} = \frac{[y_2+\beta(y_2T_{R,11}-y_1T_{R,21})\mathbf{I}y_1+\beta(y_1T_{R,22}-y_2T_{R,12})] + \beta^2\left(y_2T_{I,11}-y_1T_{I,21}+\frac{\gamma}{\beta\omega}\right)\left(y_1T_{I,22}-y_2T_{I,12}+\frac{\gamma}{\beta\omega}\right)}{[y_1+\beta(y_1T_{R,22}-y_2T_{R,12})]^2 + \beta^2\left(y_1T_{I,22}-y_2T_{I,12}+\frac{\gamma}{\beta\omega}\right)^2} \tag{41o}$$

$$R_{I,21} = \frac{\beta[y_1+\beta(y_1T_{R,22}-y_2T_{R,12})]\left(y_2T_{I,11}-y_1T_{I,21}+\frac{\gamma}{\beta\omega}\right) - \beta[y_2+\beta(y_2T_{R,11}-y_1T_{R,21})]\left(y_1T_{I,22}-y_2T_{I,12}+\frac{\gamma}{\beta\omega}\right)}{[y_1+\beta(y_1T_{R,22}-y_2T_{R,12})]^2 + \beta^2\left(y_1T_{I,22}-y_2T_{I,12}+\frac{\gamma}{\beta\omega}\right)^2} \tag{41p}$$

the crossover frequency between the out-of-phase functions of two components.

Fig. 2 shows the frequency response of the semibatch adsorber (γ=0) when the cross-terms of diffusivity and equilibrium constant are zero (D_{12}=D_{21}=0 and K_{12}=K_{21}=0). In this case, the behaviour of the frequency response of each component is independent of each other. The in-phase function of each component does not exceed unity and the out-of-function is always positive.

The in-phase and out-of-phase functions for the continuous-flow adsorber are shown in Figs. 3 and 4, respectively. As shown in Fig. 3, the value of rise frequency of the in-phase function, at which the in-phase function starts to rise above unity, is largely affected by

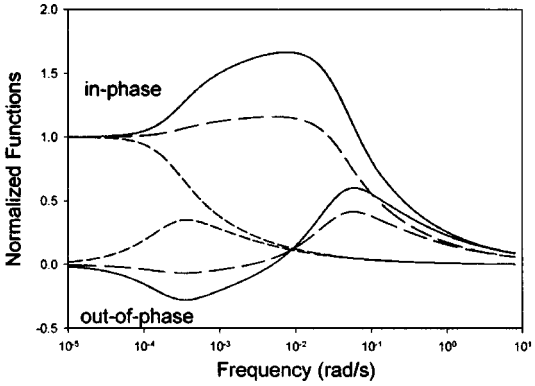

Fig. 1. Normalized in-phase and out-of-phase functions of frequency response for the reference case [CO_2 (solid), C_2H_6 (short dash), Total (long dash)].

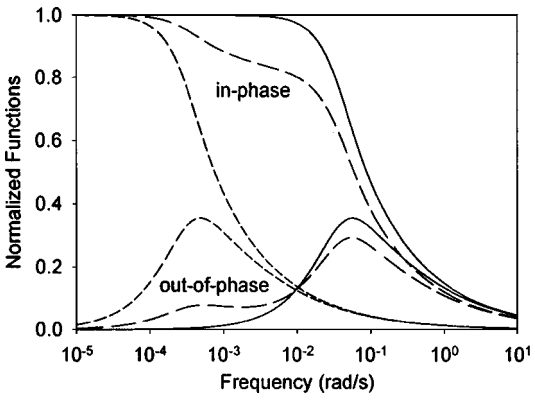

Fig. 2. Normalized in-phase and out-of-phase functions of frequency response for $D_{12}=D_{21}=K_{12}=K_{21}=0$ [CO_2 (solid), C_2H_6 (short dash), Total (long dash)].

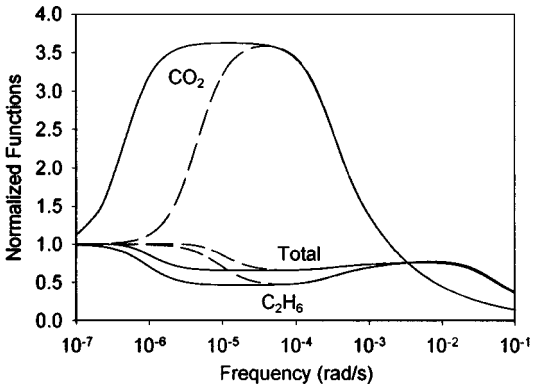

Fig. 3. Normalized in-phase functions of frequency response [$\gamma/\beta=0.0001$ (solid), $\gamma/\beta=0.001$ (dash)].

the overflow parameter. However, the decreasing part of this function seems to be unaffected by the overflow parameter. As we can see in Fig. 4, the out-of-phase function is much more sensitive to the overflow parameter than the in-phase function. The out-of-phase function for CO_2 shows a maximum and minimum in Fig. 4. At the minimum point of the out-of-phase function, the rate of increase in the diffusion term equals the rate of decrease in the overflow term. As the value of overflow parameter γ increases, the de-

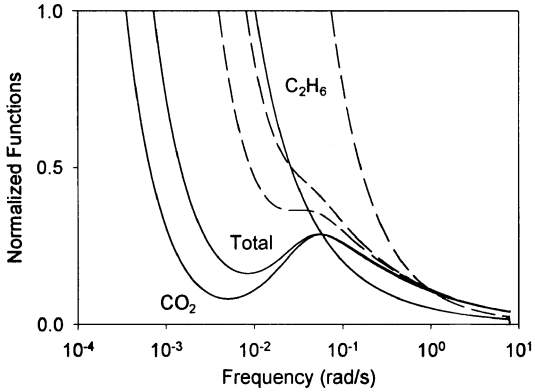

Fig. 4. Normalized out-of-phase functions of frequency response [$\gamma/\beta=0.0001$ (solid line), $\gamma/\beta=0.001$ (dash)].

viation between minimum and maximum points of the out-of-phase functions becomes smaller and smaller, then the extrema themselves vanish at some higher value of γ. Hence, it might be important to keep the overflow parameter at lower values when determining adsorption parameters using the minimum and maximum properties (e.g., using deviation of concentrations or frequencies between minimum and maximum points) of the out-of-phase functions [Park et al., 1998b]. On the other hand, the out-of-phase function for C_2H_6 for the parameter values of Fig. 4 shows no extrema at all. This is because the overflow process rather than the diffusion process in this case limits the out-of-phase function of C_2H_6.

Fig. 5 shows the out-of-phase function of the continuous-flow adsorber when the cross-terms of diffusivity and equilibrium constant are zero ($D_{12}=D_{21}=0$ and $K_{12}=K_{21}=0$). Note that the in-phase function for this case is not affected by the overflow parameter (not shown in the figure). Comparing the curves in Fig. 5 with those in Fig. 4, we see that the minimum points of the out-of-phase functions of CO_2 and total concentrations appear at slightly higher frequencies in case of non-zero cross-term diffusivities (i.e., in case of Fig. 4) when the overflow is relatively small.

Fig. 6 shows the out-of-phase function for the continuous-flow adsorber when the cross-terms of diffusivity are zero. The in-phase function in this case is not affected by the overflow parameter (not shown in the figure). Note that the same result was obtained in case

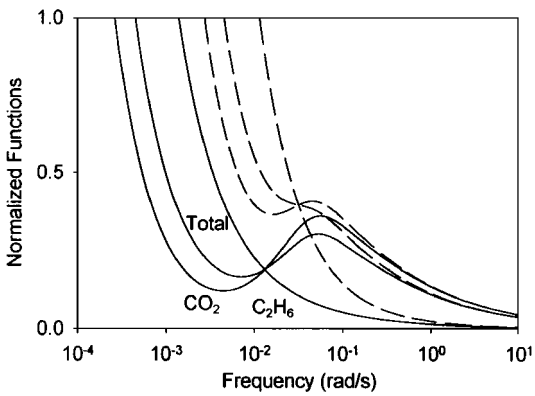

Fig. 5. Normalized out-of-phase functions of frequency response for $D_{12}=D_{21}=K_{12}=K_{21}=0$ [$\gamma/\beta=0.0001$ (solid), $\gamma/\beta=0.001$ (dash)].

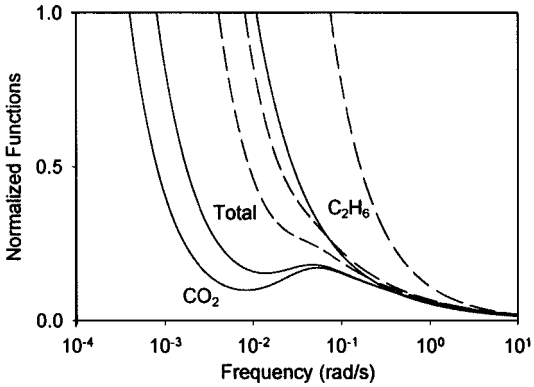

Fig. 6. Normalized out-of-phase functions of frequency response for $D_{12}=D_{21}=0$ [$\gamma/\beta=0.0001$ (solid), $\gamma/\beta=0.001$ (dash)].

of Fig. 5 (i.e., $D_{12}=D_{21}=0$ and $K_{12}=K_{21}=0$). Hence we can conclude that the in-phase function of the continuous-flow adsorber is identical with that function of the semibatch adsorber when the diffusion interference is neglected (i.e., $D_{12}=D_{21}=0$).

Other effects of the diffusion interference can be understood by comparing Fig. 6 ($D_{12}=D_{21}=0$) with Fig. 4. Due to the diffusion interference (in case of Fig. 4), the minimum point of the out-of-phase function appears at much lower frequency (for CO_2 and total concentrations), and the deviation between the maximum and the minimum becomes much larger.

Effects of equilibrium interference can be understood by comparing Fig. 6 ($D_{12}=D_{21}=0$) with Fig. 5 ($D_{12}=D_{21}=0$ and $K_{12}=K_{21}=0$). Due to the equilibrium interference (in case Fig. 6), the minimum point of the out-of-phase function appears at much higher frequency (for CO_2 and total concentrations), and the deviation between the maximum and the minimum becomes much smaller.

Due to these compensating effects of diffusion and equilibrium interferences, the minimum points of the curves in Fig. 5 appear at comparable frequencies with those in Fig. 4, and the deviations between the maximum and the minimum in Fig. 5 are also comparable with those in Fig. 4.

Contrary to the behavior of the out-of-phase function of the faster diffusing component, the out-of-phase function of the slower diffusing component shows no extrema at all for the given values of γ in this work.

CONCLUSION

In this paper, we presented a theoretical analysis of the frequency response of a continuous-flow adsorber with the periodic modulation of the inlet flow-rate to measure multicomponent diffusion kinetics in porous media. When the value of the overflow parameter is zero, the frequency response of the continuous-flow adsorber obtained in this study reduces to those of semibatch adsorbers. Micropore diffusion kinetics is assumed for the intraparticle mass transfer mechanism. Three different shapes of microparticle are considered: slab, cylinder, and sphere.

For the continuous-flow adsorber, simulation results for the binary system show that the frequency response of the faster diffusing component is strongly influenced by the slower component. The out-of-phase characteristic function of the frequency response of the faster diffusing component shows maximum and minimum points.

Due to the diffusion interference, the minimum point of the out-of-phase function appears at much lower frequency, and the deviation between the maximum and the minimum becomes much larger. Due to the equilibrium interference, the minimum point of the out-of-phase function appears much higher, and the deviations between the maximum and the minimum become much smaller.

The in-phase characteristic function of the frequency response of the continuous-flow adsorber is not affected by the overflow parameter when the diffusion interference is neglected.

NOMENCLATURE

C, C_μ : concentrations in the reservoir and micropores, respectively [mol/m^3]
$\langle C_\mu \rangle$: volumetric average of C_μ [mol/m^3]
D : effective diffusivity in micropores [m^2/s]
$F(s)$: transfer function, defined by Eq. (24)
$G(s)$: overall transfer function, defined by Eq. (29)
K : adsorption equilibrium constant
N : inlet molar flow rate to reservoir [mol/s]
q : volumetric overflow rate from reservoir [m^3/s]
$Q(s)$: transfer function for the particle, defined by Eq. (26)
r : coordinate variable of microparticle [m]
R_μ : equivalent radius of microparticle [m]
s : Laplace variable [1/s]
t : time variable [s]
$T(s)$: transfer function, defined by Eq. (23)
V, V_μ : volumes of reservoir and micropores, respectively [m^3]
$X(t)$: nondimensional forcing function
y : molar fraction of inlet stream to reservoir

Greek Letters

α : intensity parameter measuring the magnitude of the molar supply into the reservoir, N/V
β : capacity parameter, V_μ/V
γ : overflow parameter, q/V
δ_R, δ_I : in-phase and out-of-phase characteristic function for the transfer function F(s), defined by Eq. (39)
η_R, η_I : in-phase and out-of-phase characteristic function of frequency response, defined by Eq. (40)
ν : amplitude of modulation of inlet molar flow rate
σ : shape factor of particle (0 for slab, 1 for cylinder and 2 for sphere)
ω : angular frequency of the perturbation in flow rate [rad/s]

Mathematical Function

$I_n(z)$: modified Bessel function of the first kind of order n

Superscript

– : variables in the Laplace domain

Subscript

i, j, k : component index

Matrix and Vector Notation

Boldface letters : vectors of dimension n

[ ] : square matrix of dimension n×n

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