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NOTE

MOMENT EQUATION FOR THE PACKED COLUMN WITH SPHERICAL COMPOSITES

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Abstract—A mathematical model was proposed to describe the mass-transport phenomena in packed column with spherical composites which are consisted of the outer shells and the inner spheres. Any contact resistance between the former and the latter was assumed to be negligible. The first and the second moments were derived by means of the moment generating properties of Laplace transform.

INTRODUCTION

Much effort has been directed toward theory and measurement of transport properties of the packed column with porous or nonporous spherical particles. Schneider and Smith [1] considered monodispersed porous particles. Haynes and Sarma [2], and Kawazoe et al. [3] considered bidispersed porous particles. A related problem is to describe analytically the diffusion of mass or the conduction of heat through a porous medium composed of spherical composites [4, 5]. Romdhane and Danner [6] considered spherical particles with impermeable inner spheres.

Since it is generally impossible to derive the exact analytical solution in time domain for the packed column, numerical solutions by employing Fourier transform algorithm are often used to obtain informations on the transport phenomena in the packed column with particles [7]. An alternate way of obtaining analytical informations on the packed column is to make use of the moment generating properties of Laplace transform [1-3, 6].

In this note, we are going to propose a model to interpret the mass-transport phenomena of a chromatographic elution in the packed column with spherical composites. Transport properties of the outer shell are assumed to be different from those of the inner sphere. A limiting case of this model is of monodispersed porous particles.

MODELLING AND SOLUTION IN LAPLACE DOMAIN

We consider a chromatographic elution in the packed column with spherical composites. For mathematical setup of the model, the following assumptions are made:

(1) The system is consisted of the void space of the column, the outer spherical shells, and the inner spheres of the composites, the corresponding fractional volumes are ε, ε_1, and ε_2.

(2) The system is isothermal.

(3) The sizes of all the spherical composites in the column are constant; the thickness of the outer shell and the radius of inner sphere of the composite are constant.

(4) The outer shell and the inner sphere are homogeneous, respectively.

(5) No surface adsorption occurs at any interface and within any phase of the system.

(6) There are no contact resistances at the interface between the outer shell and inner sphere of the composite.

(7) Diffusion coefficients are independent of concentration.

(8) Pressure-driven flows in the composites are absent.

(9) The concentration at column inlet can be expressed as Dirac delta function.

The above assumptions are generally valid in modelling a chromatographic column packed with porous particles for the elution of nonadsorbable gases [1-3, 6, 7].

1. Model for spherical composite with permeable inner sphere

The differential mass balances and the initial and boundary conditions based upon the above assump-

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tions are as follows:

On the void space of the column;

$$D_{ax}\frac{\partial^2 C}{\partial z^2} - v\frac{\partial C}{\partial z} - \frac{3\varepsilon_2}{r_o\varepsilon}D_2\left(\frac{\partial q_2}{\partial z}\right)_{r=r_o} = \frac{\partial C}{\partial t},\quad (0<z<\infty) \tag{1}$$

On the outer shell of the spherical composite;

$$D_2\left(\frac{\partial^2 q_2}{\partial r^2} + \frac{2}{r}\frac{\partial q_2}{\partial r}\right) = \frac{\partial q_2}{\partial t},\quad (r_s<r<r_o) \tag{2}$$

On the inner sphere of the spherical composite;

$$D_1\left(\frac{\partial^2 q_1}{\partial r^2} + \frac{2}{r}\frac{\partial q_1}{\partial r}\right) = \frac{\partial q_1}{\partial t},\quad (0<r<r_s) \tag{3}$$

Initial and Boundary conditions;

$$C(z, t=0) = q_2(z, r, t=0) = q_1(z, r, t=0) = 0 \tag{4}$$

$$q_1(z, r=0, t) = \text{finite} \tag{5}$$

$$q_1(z, r=r_s, t) = q_2(z, r=r_s, t) \tag{6}$$

$$D_2\frac{\partial q_2}{\partial r} = D_1\frac{\partial q_1}{\partial r}\quad \text{at } r=r_s \tag{7}$$

$$D_2\frac{\partial q_2}{\partial r} = k_f(C-q_2)\quad \text{at } r=r_o \tag{8}$$

$$C(z=0, t) = \delta(t) \tag{9}$$

$$C(z\rightarrow\infty, t) = 0 \tag{10}$$

Among the above Eqs. (1) through (10), Eqs. (1)-(6) and Eqs. (8)-(10) are same as those of the well-known case of bidispersed porous particles in column [2, 3]. Eq. (7) is the conservation equation at the interface between the outher shell and the inner sphere of spherical composite.

The Laplace domain solution of C(z, t) can be obtained as follows:

$$\overline{C(z, p)} = \exp\{-\lambda(p)z\} \tag{11}$$

where

$$\lambda(p) = -\left(\frac{v}{2D_{ax}}\right) + \left\{\left(\frac{v}{2D_{ax}}\right)^2 + f(p)\right\}^{1/2} \tag{12}$$

$$f(p) = \frac{p}{D_{ax}} + \frac{\varepsilon_2}{\varepsilon D_{ax}}g(p) \tag{13}$$

$$g(p) = \frac{\frac{3D_2}{r_o^2}\{(\phi_3\cosh\phi_3-\sinh\phi_3)+\alpha(p)(\phi_3\sinh\phi_3-\cosh\phi_3)\}}{\frac{D_2}{r_o k_f}\{(\phi_3\cosh\phi_3-\sinh\phi_3)+\alpha(p)(\phi_3\sinh\phi_3-\cosh\phi_3)\}+\{\sinh\phi_3+\alpha(p)\cosh\phi_3\}} \tag{14}$$

$$\alpha(p) = \frac{A_2(p)-a^2A_1(p)}{a^2A_1(p)\coth\phi_2+(\coth\phi_2-\phi_2)} \tag{15}$$

$$A_1(p) = \phi_1\coth\phi_1 - 1 \tag{16}$$

$$A_2(p) = \phi_2\coth\phi_2 - 1 \tag{17}$$

$$\phi_1(p) = r_s\sqrt{p/D_1} \tag{18}$$

$$\phi_2(p) = r_s\sqrt{p/D_2} \tag{19}$$

$$\phi_3(p) = r_o\sqrt{p/D_2} \tag{20}$$

$$a = \sqrt{D_1/D_2} \tag{21}$$

2. Model for spherical composite with impermeable inner sphere

In the model for the spherical composite with impermeable inner sphere, it is reasonable to use the diffusivity D_2 based on the volume of the outer shell rather than that based on the volume of the composite. Thus, the differential mass balance on the void space of the column is

$$D_{ax}\frac{\partial^2 C}{\partial z^2} - v\frac{\partial C}{\partial z} - \frac{3r_o^2\varepsilon_2}{(r_o^3-r_s^3)\varepsilon}D_2\left(\frac{\partial q_2}{\partial z}\right)_{r=r_o} = \frac{\partial C}{\partial t},\quad (0<z<\infty) \tag{22}$$

Because the interface at $r=r_s$ is impermeable, boundary conditions (6) and (7) should be replaced by

$$q_1(z, r, t) = 0 \tag{23}$$

$$\frac{\partial q_2}{\partial r} = 0\quad \text{at } r=r_s \tag{24}$$

Eqs. (2), (3), and (22) can be solved in Laplace domain by using the initial and boundary conditions (4), (5), (8)-(10), (23), and (24) as follows:

$$\overline{C(z, p)} = \exp\{-\lambda(p)z\} \tag{11}$$

where

$$\lambda(p) = -\left(\frac{v}{2D_{ax}}\right) + \left\{\left(\frac{v}{2D_{ax}}\right)^2 + f(p)\right\}^{1/2} \tag{12}$$

$$f(p) = \frac{p}{D_{ax}} + \frac{\varepsilon_2}{\varepsilon D_{ax}}g(p) \tag{13}$$

$$g(p) = \frac{\frac{3D_2 r_o}{r_o^3-r_s^3}\{(\phi_3\cosh\phi_3-\sinh\phi_3)+\alpha(p)(\phi_3\sinh\phi_3-\cosh\phi_3)\}}{\frac{D_2}{r_o k_f}\{(\phi_3\cosh\phi_3-\sinh\phi_3)+\alpha(p)(\phi_3\sinh\phi_3-\cosh\phi_3)\}+\{\sinh\phi_3+\alpha(p)\cosh\phi_3\}} \tag{25}$$

$$\alpha(p)=\frac{A_2(p)}{\coth\phi_2-\phi_2} \quad (26)$$

where $A_2(p)$, ϕ_2, and ϕ_3 are given in Eqs. (19), (21), and (22), respectively.

Romdhane and Danner [6] reported a little different form of solution from the above equations, because they used $(\varepsilon_2/\varepsilon)\partial/\partial t(\int_{rs}^{ro} r^2q_2dr/\int_{rs}^{ro} r^2dr)$ as the third term in Eq. (22). When the partition coefficient is unity, their solution can be rearranged in the same form as Eq. (11), however, their expression of g(p) is as follows:

$$g(p)=\frac{\frac{3D_2r_o}{r_o^3-r_s^3}\{(\phi_3\cosh\phi_3-\sinh\phi_3)-(\phi_2\cosh\phi_2-\sinh\phi_2)+\alpha(p)\{(\phi_3\sinh\phi_3-\cosh\phi_3)-(\phi_2\sinh\phi_2-\cosh\phi_2)\}]}{\frac{D_2}{r_ok_f}\{(\phi_3\cosh\phi_3-\sinh\phi_3)+\alpha(p)(\phi_3\sinh\phi_3-\cosh\phi_3)\}+\{\sinh\phi_3+\alpha(p)\cosh\phi_3\}} \quad (27)$$

MOMENT EQUATIONS

1. Model for spherical composite with permeable inner sphere

The first absolute and the second central moments can be generated by the following moment generating properties of Laplace transform with Eq. (11).

$$\mu_1=(-1)\lim_{p\to 0}\frac{d\bar{C}}{dp} \quad (28)$$

$$\mu_2'=\lim_{p\to 0}\frac{d^2C}{dp^2}-\mu_1^2 \quad (29)$$

The resultant equations of μ_1 and μ_2' can be derived as follows:

$$\mu_1=\frac{z}{v}\left(1+\frac{\varepsilon_2}{\varepsilon}\right) \quad (30)$$

$$\mu_2'=\frac{2z}{v}(\delta_d+\delta_f+\delta_2+\delta_1) \quad (31)$$

where

$$\delta_d=\left(\frac{D_{ax}}{v^2}\right)\left(1+\frac{\varepsilon_2}{\varepsilon}\right)^2 \quad (32)$$

$$\delta_f=\left(\frac{r_o}{3k_f}\right)\left(\frac{\varepsilon_2}{\varepsilon}\right) \quad (33)$$

$$\delta_2=\left(\frac{r_o^2}{15D_2}\right)\left(\frac{\varepsilon_2}{\varepsilon}\right)\xi_{21} \quad (34)$$

$$\delta_1=\left(\frac{r_s^2}{15D_1}\right)\left(\frac{\varepsilon_2}{\varepsilon}\right)\xi_{11} \quad (35)$$

$$\xi_{21}=\frac{(r_o/r_s)^5-1}{(r_o/r_s)^5} \quad (36)$$

$$\xi_{11}=\frac{1}{(r_o/r_s)^3} \quad (37)$$

The above moment expressions are comparable to those of bidispersed porous particles [2, 3]: The expressions of μ_1, δ_d, and δ_f are identical to each counterpart, however, those of δ_2 [Eq. (34)] and δ_1 [Eq. (35)] have additional multiplying factors.

2. Model for spherical composite with impermeable inner sphere

With both the solution derived in this note and that presented by Romdhane and Danner [6], the same expressions of the first and the second moments can be derived as follows:

$$\mu_1=\frac{z}{v}\left(1+\frac{\varepsilon_2}{\varepsilon}\right) \quad (30)$$

$$\mu_2'=\frac{2z}{v}(\delta_d+\delta_f+\delta_2) \quad (38)$$

where

$$\delta_d=\left(\frac{D_{ax}}{v^2}\right)\left(1+\frac{\varepsilon_2}{\varepsilon}\right)^2 \quad (32)$$

$$\delta_f=\left(\frac{r_o}{3k_f}\right)\left(\frac{\varepsilon_2}{\varepsilon}\right)\xi_f \quad (39)$$

$$\delta_2=\left(\frac{r_o^2}{15D_2}\right)\left(\frac{\varepsilon_2}{\varepsilon}\right)\xi_{22} \quad (40)$$

$$\xi_f=1-\left(\frac{r_s}{r_o}\right)^3 \quad (41)$$

$$\xi_{22}=\frac{5}{2}-\frac{3/2\{(r_o/r_s)^5-1\}}{(r_o/r_s)^5-(r_o/r_s)^2}+(15)\left(\frac{r_s}{r_o}\right)^3\left[\frac{1}{3}-\frac{1/2\{(r_o/r_s)^5-(r_o/r_s)^3\}}{(r_o/r_s)^5-(r_o/r_s)^2}\right] \quad (42)$$

The above moment expressions are comparable to those of momodispersed porous particles [1]: The expressions of μ_1 and δ_d are identical to each counterpart, however, those of δ_f [Eq. (39)] and δ_2 [Eq. (40)] have additional multiplying factors. The above expression of the second central moment is different from that of Romdhane and Danner [6].

LIMITING CASE

The expressions of μ_2' are dependent of the ratio of radius of the outer shell to that of the inner sphere of the spherical composite. Taking the limit as $r_s \to 0$, we can easily obtain $\xi_{11} = \xi_{21} = \xi_f = \xi_{22} = 1$ and $\xi_{11} = 0$. Thus, the moment expressions derived in this study converge to those of monodispersed porous particles in column when $r_s \to 0$. This is sound in physical meaning.

NOMENCLATURE

- $C(z, t)$: concentration in void space of column
- $\overline{C(z, p)}$: Laplace transform of $C(z, t)$
- D_1 : diffusion coefficient in inner sphere of spherical composite
- D_2 : diffusion coefficient in outer shell of spherical composite
- D_{ax} : axial dispersion coefficient in void space of column
- k_f : mass transfer coefficient, defined by Eq. (8)
- p : Laplace domain variable
- q_1 : concentration in inner sphere of spherical composite
- q_2 : concentration in outer shell of spherical composite
- r : radial variable in spherical composite
- r_o : radius of outer shell of spherical composite
- r_s : radius of inner sphere of spherical composite
- t : time variable
- v : interstitial fluid velocity in void space of column
- z : axial variable in column

Greek Letters

- ε : fractional volume of void space of column
- ε_1 : fractional volume of inner sphere of spherical composite
- ε_2 : fractional volume of outer shell of spherical composite
- μ_1 : the first absolute moment of $C(z, t)$
- μ_2' : the second central moment of $C(z, t)$

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