研 究 速 報

UDC 541.183.21
543.544

CHROMATOGRAPHIC MOMENTS FOR PACKED BEDS OF BI-DISPERSED ADSORBENTS

二元細孔構造を有する吸着剤充塡層におけるクロマトグラフのモーメント解

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1. Introduction

This note is concerned with the analytical solutions of the moments of the chromatographic elution curve of a packed bed of bi-dispersed adsorbent particles.

Concept of bi-dispersed pore structure is shown in Figure 1. A particle of radius R is an agglomerate of microparticles of radius a which has micropores. The spaces between microparticles remain as macropores. In most cases, the size of microparticles and then the size of macropores are of the order of several micrometers. The size of a micropore is sometimes of the same order with the size of diffusing molecules while it is often of the order of several to several tens ångstrom, (1, 2, 3). In such cases, the diffusion in micropores becomes a very slow rate process and then the time constant of diffusion in a microparticle will possibly be big enough to be detected by a chromatographic technique.

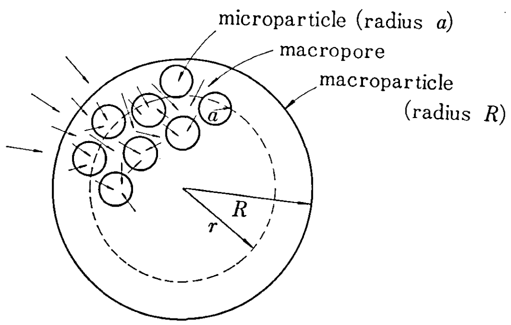

Fig. 1 Concept of Diffusion in a particle of bi-dispersed pore structure

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2. Adsorption and diffusion kinetics in microparticles

It is assumed that microparticls are solely responsible for adsorption capacity. The diffusion into microparticles can be classified into two typical kinetics.

Model I: The molecules are adsorbed at the external surface of the microparticles and then adsorbed molecule diffuses into microparticles. In this case the driving force of the diffusion will be the gradient of the concentration of adsorbed molucules, q. Figure 2 shows an illustration for this situation.

$$N_1=k_s\left(c_a-\frac{q|_{r_i=a}}{K^*}\right)=D\frac{\rho_p}{1-\varepsilon_a}\frac{\partial q}{\partial r_i}\bigg|_{r_i=a} \tag{1}$$

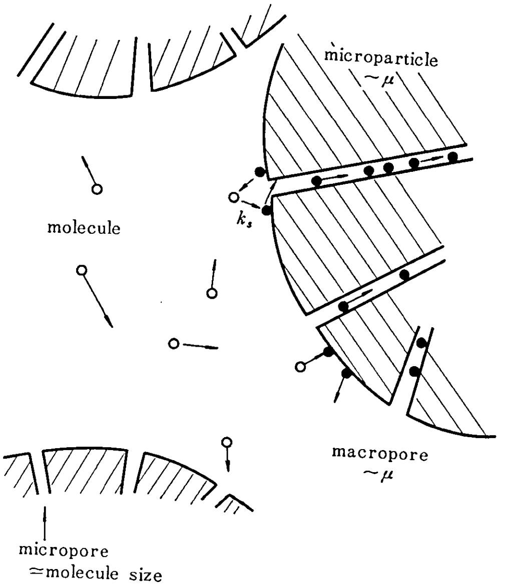

Fig. 2 Particle surface adsorption and sorption in microparticles (Model I)

$$D\left(\frac{\partial^2 q}{\partial r_i^2}+\frac{2}{r_i}\frac{\partial q}{\partial r_i}\right)=\frac{\partial q}{\partial t} \qquad (2)$$

In most molecular sieving material, these equations may be more descriptive than a model shown later.

Madel II: The driving force of diffusion will be gas phase concentration gradient in micropore and the diffusion is followed by adsorption at the micropore wall. This idea is schematically shown in Figure 3.

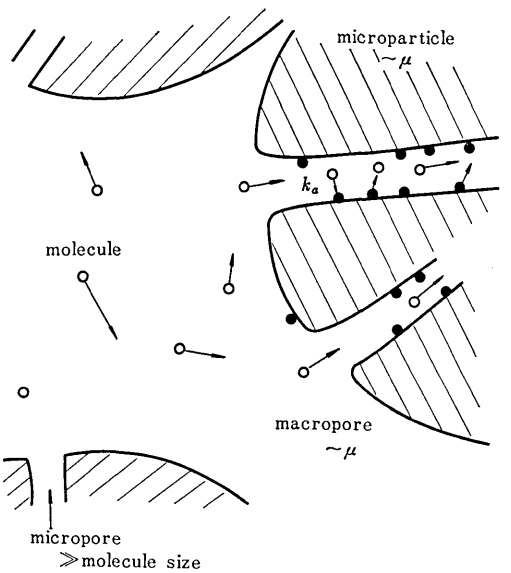

Fig. 3 Gas phase diffusion and pore surface adsorption in micropore (Model II)

In this case the equations describing the above mentioned processes will be:

$$N_1=D_i\frac{\partial c_i}{\partial r_i}\bigg|_{r_i=a}, \quad c_a=c_i|_{r_i=a} \qquad (3)$$

$$\frac{D_i}{\varepsilon_i}\left(\frac{\partial^2 c_i}{\partial r_i^2}+\frac{2}{r_i}\frac{\partial c_i}{\partial r_i}\right)-\frac{1}{\varepsilon_i}N_2=\frac{\partial c_i}{\partial t} \qquad (4)$$

$$N_2=\rho_i k_a\left(c_i-\frac{n}{K_a}\right)=\rho_i\frac{\partial n}{\partial t} \qquad (5)$$

When micropore is reasonably large compared with diffusing molecules, gas phase diffusion can be controlling. Then this situation will be realistic for ordinary bi-dispersed systems rather than molecular sieving materials.

3. Basic equations in a packed bed

Material balances in a packed bed, at the exteral surface of the particles, inside the macroparticle are as follows

$$E_z\frac{\partial^2 c}{\partial z^2}-u\frac{\partial c}{\partial z}-\frac{3(1-\varepsilon)}{\varepsilon R}N_0=\frac{\partial c}{\partial t} \qquad (6)$$

$$N_0=k_f(c-c_a|_{r=R})=D_a\frac{\partial c_a}{\partial r}\bigg|_{r=R} \qquad (7)$$

$$\frac{D_a}{\varepsilon_a}\left(\frac{\partial^2 c_a}{\partial r^2}+\frac{2}{r}\frac{\partial c_a}{\partial r}\right)-\frac{3(1-\varepsilon_a)}{\varepsilon_a a}N_1=\frac{\partial c_a}{\partial t} \qquad (8)$$

Impulse input is taken as the boundary condition at the inlet of the bed

$$\left.\begin{array}{ll} z=0 & c=M\delta(t) \\ z=\infty & c=0 \end{array}\right\}. \qquad (9)$$

4. Solution in the Laplace domain

Model I: For Model I, Eqs. (1) and (2) combined with Eqs. (6)～(9) can be solved in Laplace domain. Let $\bar{c}$, $\bar{c}_a$, $\bar{q}$, $\bar{N}_0$ and $\bar{N}_1$ be the transformed c, c_a, q, N_0 and N_1, and Eqs. (1)′, (2)′, (6)′, (7)′, (8)′ and (9)′ be the transformed version of Eqs. (1), (2), (6), (7), (8) and (9).

$$E_z\frac{\partial^2 \bar{c}}{\partial z^2}-u\frac{\partial \bar{c}}{\partial z}-\frac{3(1-\varepsilon)}{\varepsilon\cdot R}\bar{N}_0=p\bar{c} \qquad (6)'$$

$$\bar{N}_0=k_f(\bar{c}-\bar{c}_a|_{r=R})=D_a\frac{\partial \bar{c}_a}{\partial r}\bigg|_{r=R} \qquad (7)'$$

$$\frac{D_a}{\varepsilon_a}\left(\frac{\partial^2 \bar{c}_a}{\partial r^2}+\frac{2}{r}\frac{\partial \bar{c}_a}{\partial r}\right)-\frac{3(1-\varepsilon_a)}{\varepsilon_a a}\bar{N}_1=p\bar{c}_a \qquad (8)'$$

$$\bar{N}_1=k_s\left(\bar{c}_a-\frac{\bar{q}|_{r_i=a}}{K^*}\right)=D\frac{\rho_p}{1-\varepsilon_a}\frac{\partial \bar{q}}{\partial r_i}\bigg|_{r_i=a} \qquad (1)'$$

$$D\left(\frac{\partial^2 \bar{q}}{\partial r_i^2}+\frac{2}{r_i}\frac{\partial \bar{q}}{\partial r_i}\right)=p\bar{q} \qquad (2)'$$

$$z=0 \qquad \bar{c}=M \qquad (9)'$$

The moments of the impulse response can be related to the solution in the Laplace domain (4, 5), which will be tried to obtain first. The solution for $\bar{q}$ from Eq. (2)′, in terms of $B_1(z, r)$ (a function of z and r to be evaluated later), is

$$\bar{q}=\frac{B_1(z, r)}{r_i}\sinh(r_i\sqrt{p/D}) \qquad (10)$$

The concentration in the macropore can be established by substituting Eq. (10) into the last two members of Eq. (1)′:

$$\bar{c}_a=\frac{B_1(z,r)}{B_iK^*}\cdot\frac{\sinh\phi_1(p)}{a}\{A_1(p)+B_i\} \quad (11)$$

where

$$\phi_1(p)=a\sqrt{p/D} \quad (12)$$

$$A_1(p)=\phi_1(p)\coth\phi_1(p)-1 \quad (13)$$

$$B_i=\frac{(1-\varepsilon_a)}{\rho_pK^*}\cdot\frac{k_sa}{D} \quad (14)$$

Equation (10) can be used to evaluate $\bar{q}$ and $(\partial\bar{q}/\partial r_i)$ at $r_i=a$. These results can be sabstituted, along with $\bar{c}_a$ from Eq. (11), into Eq. (1)′ to obtain $\bar{N}_1$ in terms of z and r. Introducing this relation for $\bar{N}_1$ into Eq. (8)′ yields

$$\frac{D_a}{\varepsilon_a}\left\{\frac{\partial^2B_1(z,r)}{\partial r^2}+\frac{2}{r}\frac{\partial B_1(z,r)}{\partial r}\right\}=\kappa_2(p)\cdot B_1(z,r) \quad (15)$$

where

$$\kappa_2(p)=p+\frac{3(1-\varepsilon_a)}{\varepsilon_aa/k_s}\left[1-\frac{B_i}{A_1(p)+B_i}\right] \quad (16)$$

Then $B_1(z,r)$ can be solved to give

$$B_1(z,r)=\frac{B_2(z)}{r}\sinh\{r\sqrt{\varepsilon_a\cdot\kappa_2(p)/D_a}\} \quad (17)$$

The concentration in the interparticle gas can be established by substituting Eq. (11) and (17) into the last two members of Eq. (7)′:

$$\bar{c}=\frac{B_2(z)}{B_aB_iK^*}\cdot\frac{\sinh\phi_1(p)\sinh\phi_2(p)}{aR}\times\{A_1(p)+B_i\}\{A_2(p)+B_a\} \quad (18)$$

where

$$\phi_2(p)=R\sqrt{\varepsilon_a\kappa_2(p)/D_a} \quad (19)$$

$$A_2(p)=\phi_2(p)\coth\phi_2(p)-1 \quad (20)$$

$$B_a=\frac{k_fR}{D_a} \quad (21)$$

Equation (11), along with Eq. (17), can be used to evaluate $\bar{c}_a$ and $(\partial\bar{c}_a/\partial r)$ at $r=R$. These results can be substituted, along with $\bar{c}$ from Eq. (18), into Eq. (7)′ to obtain $\bar{N}_0$ in terms of z. Introducing this relation for $\bar{N}_0$ into Eq. (6)′ yields

$$E_z\frac{\partial^2B_2(z)}{\partial z^2}-u\frac{\partial B_2(z)}{\partial z}-G(p)B_2(z)=0 \quad (21)$$

where

$$G(p)=p+\frac{3(1-\varepsilon)}{\varepsilon\cdot R/k_f}\left[1-\frac{B_a}{A_2(p)+B_a}\right] \quad (22)$$

The solution of Eq. (21) gives

$$B_2(z)=B_0\exp\{-\lambda(p)z\} \quad (23)$$

$$\lambda(p)=\frac{u}{2E_z}\left[\sqrt{1+\frac{4E_z}{u^2}G(p)}-1\right] \quad (24)$$

The expression for $\bar{c}$ is Eq. (18) with $B_2(z)$ from Eq. (23), or

$$\bar{c}=\frac{B_0}{B_aB_iK^*}\exp\{-\lambda(p)z\}\frac{\sinh\phi_1(p)\sinh\phi_2(p)}{aR}\times\{A_1(p)+B_i\}\{A_2(p)+B_a\} \quad (25)$$

Then, using the initial condition, Eq. (9)′, the final equation of $\bar{c}(p)$ becomes

$$\bar{c}(p)=M\exp\{-\lambda(p)z\} \quad (26)$$

$$\left.\begin{aligned}&\lambda(p)=\frac{u}{2E_z}\left[\sqrt{1+\frac{4E_z}{u^2}G(p)}-1\right]\\&G(p)=p+\frac{3(1-\varepsilon)}{\varepsilon R/k_f}\left[1-\frac{B_a}{A_2(p)+B_a}\right]\\&A_2(p)=\phi_2(p)\coth\phi_2(p)-1\\&\phi_2(p)=R\sqrt{\varepsilon_a\kappa_2(p)/D_a}\\&\kappa_2(p)=p+\frac{3(1-\varepsilon_a)}{\varepsilon_a\cdot a/k_s}\left[1-\frac{B_i}{A_1(p)+B_i}\right]\\&A_1(p)=\phi_1(p)\coth\phi_1(p)-1\\&\phi_1(p)=a\sqrt{p/D}\end{aligned}\right\} \quad (27)$$

Model II: For Model II, Eqs. (3)∼(9) can be solved in Laplace domain. The transforms of Eqs. (3)∼(5) are

$$\bar{N}_1=D_i\left.\frac{\partial\bar{c}_i}{\partial r_i}\right|_{r_i=a}\quad \bar{c}_a=\bar{c}_i|_{r_i=a} \quad (3)'$$

$$\frac{D_i}{\varepsilon_i}\left(\frac{\partial^2\bar{c}_i}{\partial r_i^2}+\frac{2}{r_i}\frac{\partial\bar{c}_i}{\partial r_i}\right)-\frac{1}{\varepsilon_i}\bar{N}_2=p\bar{c}_i \quad (4)'$$

$$\bar{N}_2=\rho_ik_a\left(\bar{c}_i-\frac{\bar{n}}{K_a}\right)=\rho_ip\bar{n} \quad (5)'$$

Eqs. (6)′∼(9)′ are valid here. Elimination of $\bar{n}$ from Eqs. (4)′ and (5)′ give

$$\frac{D_i}{\varepsilon_i}\left(\frac{\partial^2\bar{c}_i}{\partial r_i^2}+\frac{2}{r_i}\frac{\partial\bar{c}_i}{\partial r_i}\right)=\kappa_1'(p)\bar{c}_i \quad (28)$$

where

$$\kappa_1'(p)=p+\frac{\rho_ik_ap}{\varepsilon_i(p+k_a/K_a)} \quad (29)$$

Then $\bar{c}_i$ can be solved to give

$$\bar{c}_i=\frac{B_1(z,r)}{r_i}\sinh\{r_i\sqrt{\varepsilon_i\kappa_1'(p)/D_i}\} \quad (30)$$

From Eq. (3)′

$$\bar{c}_a=\frac{B_1(z,r)}{a}\sinh\phi_1'(p) \quad (31)$$

$$\phi_1'(p)=a\sqrt{\varepsilon_i\cdot\kappa_1'(p)/D_i} \quad (32)$$

Introducing Eqs. (3)′, (30) and (31) into Eq. (8)′

yields

$$\frac{D_a}{\varepsilon_a}\left(\frac{\partial^2 B_1(z,r)}{\partial r^2}+\frac{2}{r}\frac{\partial B_1(z,r)}{\partial r}\right)$$
$$=\kappa_2'(p)B_1(z,r) \tag{33}$$

where

$$\kappa_2'(p)=p+\frac{3(1-\varepsilon_a)}{\varepsilon_a\cdot a^2/D_i}\{\phi_1'(p)\coth\phi_1'(p)-1\} \tag{34}$$

Then

$$B_1(z,r)=\frac{B_2(z)}{r}\sinh\{r\sqrt{\varepsilon_a\cdot\kappa_2'(p)/D_a}\} \tag{35}$$

This is the same form as Eq. (17). Then similar treatment shown for Model I is employed to give the final result same as Eqs. (26) and (27) except that $\kappa_2'(p)$ (Eqs. (34), (32) and (29)) should be used instead of $\kappa_2(p)$ (Eqs. (16), (13) and (12)).

5. Moment equations

The moments of the impulse response are related to the transfer function, $\bar{c}(p)$, by the expression

$$m_n=\int_0^\infty c(t)t^n dt$$
$$=(-1)^n\lim_{p\to 0}\left[\left(\frac{\partial}{\partial p}\right)^n\bar{c}(p)\right] \tag{36}$$

Then the first absolure moment μ_1 is given as

$$\mu_1=\frac{m_1}{m_0}=-\lim_{p\to 0}\left[\frac{d}{dp}\bar{c}(p)\right]\Big/\bar{c}(0) \tag{37}$$

Also the second central moment μ_2' is easily related to μ_2 and μ_1

$$\mu_2'=\int_0^\infty c(t)\cdot(t-\mu_1)^2dt\Big/\int_0^\infty c(t)dt$$
$$=\int_0^\infty c(t)t^2dt\Big/\int_0^\infty c(t)dt-\mu_1^2$$
$$=\lim_{p\to 0}\left[\frac{d^2}{dp^2}\bar{c}(p)\right]\Big/\bar{c}(0) \tag{38}$$

Model I: Then the moment equations for Model I are derived by applying Eqs. (37) and (38) to Eq. (26).

$$\mu_1=\frac{z}{u}\left\{1+\frac{(1-\varepsilon)}{\varepsilon}(\varepsilon+\rho_pK^*)\right\} \tag{39}$$

$$\mu_2'=\frac{2z}{u}\{\delta_d+\delta_f+\delta_a+\delta_s+\delta_i\} \tag{40}$$

$$\left.\begin{aligned}
\delta_d&=\frac{E_z}{u^2}\left\{1+\frac{(1-\varepsilon)}{\varepsilon}(\varepsilon_a+\rho_pK^*)\right\}^2\\
\delta_f&=\frac{1-\varepsilon}{\varepsilon}\frac{R}{3k_f}(\varepsilon_a+\rho_pK^*)^2\\
\delta_a&=\frac{1-\varepsilon}{\varepsilon}\frac{R^2}{15D_a}(\varepsilon_a+\rho_pK^*)^2\\
\delta_s&=\frac{1-\varepsilon}{\varepsilon}\frac{a}{3k_s}\frac{(\rho_pK^*)^2}{(1-\varepsilon_a)}\\
\delta_i&=\frac{1-\varepsilon}{\varepsilon}\frac{a^2}{15D}\rho_pK^*
\end{aligned}\right\} \tag{41}$$

These δ can be used to check the relative importance of each transport process. Naturally, when the intra-microparticle diffusion is not significant, the resu'ts coincide with those obtained for uni-dispersed system (6).

Model II: The results for Model II are

$$\mu_1=\frac{z}{u}\left[1+\frac{(1-\varepsilon)}{\varepsilon}\{\varepsilon_a+(1-\varepsilon_a)(\varepsilon_i+\rho_iK_a)\}\right] \tag{42}$$

$$\mu_2'=\frac{2z}{u}\{\delta_d+\delta_f+\delta_a+\delta_i+\delta_{ad}\} \tag{43}$$

$$\left.\begin{aligned}
\delta_d&=\frac{E_z}{u^2}\left[1+\frac{(1-\varepsilon)}{\varepsilon}\cdot\{\varepsilon_a+(1-\varepsilon_a)(\varepsilon_i+\rho_iK_a)\}\right]^2\\
\delta_f&=\frac{1-\varepsilon}{\varepsilon}\frac{R}{3k_f}\{\varepsilon_a+(1-\varepsilon_a)(\varepsilon_i+\rho_iK_a)\}^2\\
\delta_a&=\frac{1-\varepsilon}{\varepsilon}\frac{R^2}{15D_a}\{\varepsilon_a+(1-\varepsilon_a)(\varepsilon_i+\rho_iK_a)\}^2\\
\delta_i&=\frac{1-\varepsilon}{\varepsilon}\frac{a^2}{15D_i}(1-\varepsilon_a)(\varepsilon_i+\rho_iK_a)^2\\
\delta_{ad}&=\frac{1-\varepsilon}{\varepsilon}\frac{1}{k_a}(1-\varepsilon_a)(\rho_iK_a)^2
\end{aligned}\right\} \tag{44}$$

This resu't is identical with the form shown by Kawazoe (2) and Hashimoto and Smith (7).

Notation

A_1	function of ϕ_1 defined by Eq. (13)
A_2	function of ϕ_2 defined by Eq. (20)
a	radius of micropartic'e [cm]
B_0	integration constant in Eq. (23) [cm]
$B_1(z,r)$	coefficient in Eq. (10) [cm]
$B_2(z)$	coefficiet in Eq. (17) [cm]
c	concentration in the fluid phase [mole/cc]
c_a	concentration in the macropore [mole/cc]
c_i	concentration in the micropore [mole/cc]
D	diffusivity in micropores based on amount adsorbed gradient driving force [cm^2/sec]
D_a	diffusivity in macropores [cm^2/sec]

D_i diffusivity in micropores based on gas phase concentration gradient driving force [cm^2/sec]
E_z axial dispersion coefficient base on void spaces in the bed [cm^2/sec]
$G(p)$ function defined by Eq. (22) [sec^{-1}]
K^* apparent adsorption equilibrium constant [cc/g]
K_a apparent adsorption equiiibtium constant [cc/g]
k_a adsorption rate constant [g^{-1}sec^{-1}]
k_f fluid-to-particle mass transfer coefficient [cm/sec]
k_s adsorption rate constant [cm/sec]
M intensity of injected pulse [mole·sec/cc]
m_n nth moment integral, defined by Eq. (36) [mole/cm^3·sec^n]
N_0 molal flux from fluid to particle in bed [mole/cm^2·sec]
N_1 molal flux from macropore to microparticle [mole/cm^2·sec]
N_2 molal flux from micropore to surface [mole/cm^3·sec]
n amount adsorbed [mole/g]
p Laplace transform variadle [sec^{-1}]
q amount adsorbed [mole/g]
R radius of adsorbent particle [cm]
r radial distance from center of particle [cm]
r_i radial distance from center of microparticle [cm]
t time [sec]
u average velocity in the interparticle space in the bed [cm/sec]
z axial distance in the bed [cm]

Greek symbols

$\delta_a, \delta_{ad}, \delta_d, \delta_f, \delta_i, \delta_s$ functions defined by Eqs. (41) and (44) [sec]
$\delta(t)$ delta function
ε void fraction in the bed
ε_a void fraction of macropore in the particle
ε_i void fraction of micropore in the microparticle
$\kappa_1(p)$ function defined by Eq. (29)
$\kappa_2(p)$ function defined by Eqs. (16) and (34)
$\lambda(p)$ function defined by Eq. (24)
μ_1 first absolute moment, defined by Eq. (37) [sec]
μ_2' second central moment, defined by Eq. (38) [sec^2]
ρ_i density of microparticle [g/cc]
ρ_p density of particle [g/cc]
$\phi_1(p)$ function defined by Eqs. (12) and (32)
$\phi_2(p)$ function defined by Eq. (19)

Dimensionless groups

$$B_a=\frac{k_f R}{D_a}$$

$$B_i=\frac{(1-\varepsilon_a)}{\rho_p K^*}\cdot\frac{k_s a}{D}$$

A bar over c, c_a, c_i, q, n, N_0, N_1 and N_2 denotes the Laplace transform of the variable.

A prime of κ and ϕ denotes that these functions are concerned with Model II.

(Manuscript received, October 23, 1973)

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