R & D NOTES

The Kinetics of Sorption in a Biporous Adsorbent Particle

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The problem of adsorption in a biporous particle consisting of a macroporous pellet containing an assemblage of uniform microporous adsorbent particles has been considered by Ruckenstein et al. (1971) and by Ma and Lee (1976). Ruckenstein et al. developed an expression for the uptake curve for such a particle when subjected to a step change in sorbate concentration at the external surface. Ma and Lee considered the more complex boundary condition which arises when the adsorbent particle is immersed in a well-mixed solution of finite volume. An expression for the uptake curve was obtained in Laplace form, but the transform was not inverted. This note deals with essentially the same system as was considered by Ma and Lee. The expression for the uptake curve is obtained in the time domain, and it is shown that this expression reduces to the Ruckenstein solution in the limiting case of a very large vessel. Since the derivation of the solution in Laplace form was omitted by Ma and Lee, it is given here in abbreviated form.

Subject to the usual assumptions of a linear isotherm and constant diffusivities in both macro and micropores, the kinetics of sorption in the biporous particle may be described by the following set of equations:

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(D_c r^2 \cdot \frac{\partial q}{\partial r}\right) = \frac{\partial q}{\partial t} \qquad (1)$$

$$\frac{\partial q}{\partial r}(0, t) = 0 \qquad (2)$$

$$q(r_c, t) = Kc(R, t) \qquad (3)$$

$$\overline{q}(R, t) = \frac{3}{r_c^3} \cdot \int_0^{r_c} q r^2 dr \qquad (4)$$

$$\frac{1}{R^2}\frac{\partial}{\partial R}\left(D_p R^2 \frac{\partial c}{\partial R}\right) = \frac{\partial c}{\partial t} + \left(\frac{1-\epsilon}{\epsilon}\right)\frac{\partial \overline{q}}{\partial t} \qquad (5)$$

$$\frac{\partial c}{\partial R}(0, t) = 0 \qquad (6)$$

$$c(R_p, t) = C(t) \qquad (7)$$

$$q(r, 0) = c(R, 0) = 0 \qquad (8)$$

The uptake by the particle at time t is given by

$$m_t = 3\int_0^1 [(1-\epsilon)\overline{q} + \epsilon c]\eta^2 d\eta \qquad (9)$$

and since as $t \rightarrow \infty$, $m_t \rightarrow (1-\epsilon)\overline{q}_\infty + \epsilon c_\infty$, the fractional uptake is given by

$$\frac{m_t}{m_\infty} = \frac{3}{1 + \frac{3\alpha}{\beta}(1-\Lambda)}\int_0^1 \left[\overline{Q} + \frac{3\alpha}{\beta} \cdot \frac{c}{C_o}\right]\eta^2 d\eta \qquad (10)$$

where $\Lambda = 1 - C_\infty/C_o$ is the fraction of sorbate originally present in the solution which is eventually adsorbed. Expressed in Laplace form in terms of the dimensionless variables, the diffusion equations [Equations (1) and (5)] become

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$$\frac{d^2\tilde{N}_c}{d\zeta^2} = s\tilde{N}_c \tag{11}$$

$$\frac{d^2\tilde{N}_p}{d\eta^2} = s\alpha\tilde{N}_p + \frac{\eta\beta s}{3}\tilde{\bar{Q}} \tag{12}$$

Equation (11) may be solved with boundary conditions (2) and (3) to obtain

$$\tilde{N}_c = \frac{c(1,\eta,\tau)}{C_\infty} \cdot \frac{\sinh(\zeta\sqrt{s})}{\sinh(\sqrt{s})}$$

$$= \frac{\tilde{N}_p}{\eta(1-\Lambda)} \cdot \frac{\sinh(\zeta\sqrt{s})}{\sinh(\sqrt{s})} \tag{13}$$

and on integration over a microparticle

$$\tilde{\bar{Q}} = 3\int_0^1 \left(\frac{N_c}{\zeta}\right)\zeta^2 \cdot d\zeta = \frac{3\tilde{N}_p}{\eta s(1-\Lambda)} \cdot (p\cot p - 1) \tag{14}$$

where $p^2 = -s$. Equation (12) may now be solved with Equation (14) and boundary condition (7) to yield

$$\frac{\tilde{c}}{C_o} = \frac{\tilde{N}_p}{\eta} = \frac{\tilde{C}}{C_o} \cdot \frac{\sinh[\eta u(p)]}{\eta \sinh[u(p)]} \tag{15}$$

where

$$u^2 = \frac{\beta}{1-\Lambda} \cdot (p\cot p - 1) - \alpha p^2 \tag{16}$$

The expression for the fractional uptake [Equation (10)] becomes in the Laplace form

$$\frac{\tilde{m}_t}{m_\infty} = \frac{9}{1 + \dfrac{3\alpha}{\beta}(1-\Lambda)} \int_0^1 \left\{ \frac{(p\cot p - 1)}{s(1-\Lambda)} + \frac{\alpha}{\beta} \right\} \cdot \frac{\tilde{C}}{C_o} \cdot \frac{\eta \sinh \eta u}{\sinh u} \cdot d\eta \tag{17}$$

$$= \frac{9}{\beta + 3\alpha(1-\Lambda)} \cdot \frac{u\cosh u - \sinh u}{\sinh u} \cdot \frac{1}{s} \cdot \left(\frac{\tilde{C}}{C_o}\right) \tag{18}$$

and by overall mass balance

$$\frac{\tilde{C}}{C_o} = \left[\frac{9\Lambda}{\beta + 3\alpha(1-\Lambda)} \cdot (u\coth u - 1) - p^2 \right]^{-1} \tag{19}$$

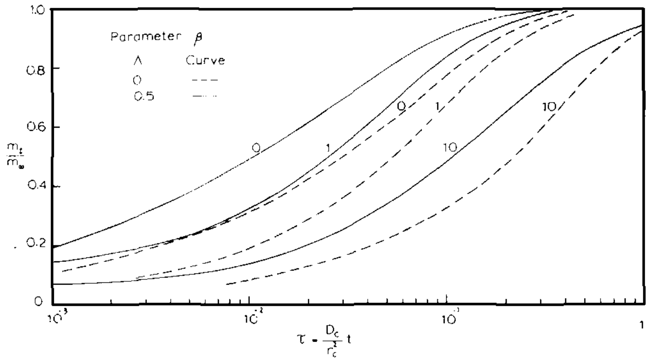

Fig. 1. Comparison of theoretical uptake curves predicted by the linear dual diffusional resistances model for the case of an infinite vessel ($\Lambda = 0$) and for the case of a finite vessel ($\Lambda = 0.5$). Curves for the infinite vessel (– – –) are given by Equations (22) and (21), while curves for the finite vessel (—) are computed from Equations (25). (28), and (29). Effects of macropore accumulation have been neglected in both cases.

This expression together with Equation (16) constitutes the solution to the problem in Laplace form. The equations may be reduced to the form given by Ma and Lee by the substitution $P = -i\sqrt{s}$, $\cot p = i \coth \sqrt{s}$. If the volume of the solution is large in comparison with the capacity of the adsorbent $\Lambda \rightarrow 0$ and $C/C_o = 1/s$, then

$$\frac{\tilde{m}_t}{m_\infty} = \frac{9}{\beta + 3\alpha} \cdot \frac{1}{s^2} \cdot \frac{u\cosh u - \sinh u}{\sinh u} \tag{20}$$

This expression has a simple pole at $s = 0$ (residue 1.0), and a series of poles at $\sinh u = 0$, $u_n = in\pi$ or $u_n^2 = -n^2\pi^2$. Equation (16) then becomes

$$\alpha p^2_{n,m} - n^2\pi^2 = \beta(p_{n,m}\cot p_{n,m-1}) \tag{21}$$

This gives the residues

$$\frac{9}{\beta + 3\alpha} \cdot \frac{e^{s\tau}}{s^2} \cdot \frac{(u\cosh u - \sinh u)}{\dfrac{d}{ds}(\sinh u)}$$

which may be reduced with the aid of Equation (21) to

$$\frac{18}{\beta + 3\alpha} \cdot \left(\frac{-n^2\pi^2}{p^4}\right) \cdot \frac{e^{-p^2\tau}}{\alpha + \dfrac{\beta}{2}\left\{1 + \dfrac{\cot p}{p}(p\cot p - 1)\right\}}$$

so that the expression for the uptake curve in the time domain is

$$\frac{m_t}{m_\infty} = 1 - \frac{18}{\beta + 3\alpha} \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \left(\frac{n^2\pi^2}{p_{n,m}{}^4}\right) \frac{e^{-p_{n,m^2}\tau}}{\alpha + \dfrac{\beta}{2}\left[1 + \dfrac{\cot P_{n,m}}{P_{n,m}}(p_{n,m}\cot p_{n,m}{}^{-1})\right]} \tag{22}$$

This expression is equivalent to the expression given by Ruckenstein et al. for a particle subjected to a step change in sorbate concentration at the external surface.

For the finite vessel case, Equations (18) and (19) give

$$\frac{\tilde{m}_t}{m_\infty} = \frac{9}{\beta + 3\alpha(1-\Lambda)} \cdot \frac{1}{s^2} \cdot \frac{u\cosh u - \sinh u}{\left\{\sinh u + \dfrac{9\gamma}{s\beta}(u\cosh u - \sinh u)\right\}} \tag{23}$$

where $\gamma = \beta\Lambda/[\beta + 3\alpha(1-\Lambda)]$. The simple pole at $s = 0$ yields, as expected, the residue 1.0. In addition there is a series of poles given by

$$\sinh u = \frac{-9\gamma}{s\beta}(u\cosh u - \sinh u) \tag{24}$$

from which the residues are obtained as

$$\left(\frac{9\gamma}{\Lambda\beta}\right)\frac{1}{s} \cdot \frac{(u\cosh u - \sinh u)e^{s\tau}}{\dfrac{d}{ds}\left\{s\sinh u + \dfrac{9\gamma}{\beta}(u\cosh u - \sinh u)\right\}}$$

This gives the expression for the uptake curve:

$$\frac{m_t}{m_\infty} = 1 + \sum_{n=1}^{\infty}\sum_{m=1}^{\infty}\left(\frac{18\gamma}{\beta\Lambda s_{n,m}}\right)\frac{u_n(u_n\cosh u_n - \sinh u_n)e^{s_{n,m}\tau}}{2u_n \sinh u_n + \left\{ s_{n,m}\cosh u_n + \frac{9\gamma}{\beta}u_n \sinh u_n \right\}\cdot \left.\frac{du^2}{ds}\right|_{s=s_{n,m}}} \tag{25}$$

where

$$\left.\frac{du^2}{ds}\right|_{s=s_{n,m}} = \alpha + \frac{\beta}{2(1-\Lambda)}\left[1 + \frac{\cot P_{n,m}}{P_{n,m}}\left(P_{n,m}\cot P_{n,m-1}\right)\right]$$

and $s_{n,m}$ are the roots of the transcendental Equations (16) and (24). The expression for the time dependence of the fluid phase concentration may be obtained directly from the overall mass balance, since $C/C_o = 1 - \Lambda(m_t/m_\infty)$. In the limiting case $\Lambda \to 0$ we have $\gamma \to 0$, $\sinh u \to 0$, $u \to in\pi$ so that Equation (16) becomes identical with Equation (21) and Equation (25) reduces to Equation (22). When Λ is finite, the solution may be expressed in the somewhat more convenient form

$$\frac{m_t}{m_\infty} = 1 - \frac{1}{\Lambda}\sum_{n=1}^{\infty}\sum_{m=1}^{\infty}\frac{e^{s_{n,m}\tau}}{1 + \frac{1}{4}\left[\frac{9\gamma}{\beta} + s_{n,m}\left(1 - \frac{\beta S_{n,m}}{9\gamma}\right)/u_n^2\right]L_{n,m}} \tag{26}$$

where

$$L_{n,m} = \left(2\alpha + \frac{\beta}{1-\Lambda}\right) + \left(\frac{u_n^2 - \alpha s_{n,m}}{s_{n,m}}\right)\left[1 + \frac{(1-\Lambda)(u_n^2 - \alpha s_{n,m})}{\beta}\right]$$

with $s_{n,m}$ given by the roots of Equation (16), and

$$u_n \coth u_n = 1 - s_{n,m}\beta/9\gamma \tag{27}$$

This expression is useful for the analysis of experimental uptake curves for liquid phase systems since in order to follow the progress of the uptake curve by monitoring the liquid phase concentration the conditions of the experiment must be chosen to ensure that the capacity of the adsorbent is comparable with the total quantity or sorbate in the solution (that is, $\Lambda >> 0$).

To illustrate the form of the solution, a set of uptake curves has been computed from Equations (26), (16), and (27) for $\Lambda = 0.5$ with β as parameter. Macropore accumulation is neglected, since this is usually a good approximation provided that the solution is dilute. The curves are shown in Figure 1 together with the corresponding curves for an infinite vessel ($\Lambda = 0$), as given by Equations (22) and (21).

There are two types of roots for the present system (Λ finite), according to whether u is real or imaginary. If we neglect macropore accumulation, Equations (16) and (27) reduce to

$$u^2 = \frac{\beta}{1-\Lambda}(p\cot p - 1) \tag{28}$$

and

$$u\coth u - 1 = P^2\beta/9\Lambda \tag{29}$$

For positive real argument u, $u \coth u - 1$ is a monotonic increasing function, while for imaginary argument the function varies periodically. Let P_n^o denote the n^{th} roots of the equation $p\cot p - 1 = 0$. For values of p lying between $(n-1)\pi$ and P_n^o, u is real; hence there is only one set of (P, u) satisfying both Equations 28 and 29. However, for values of P lying between P_n^o and $n\pi$, u is imaginary, and in principle there are infinite pairs of roots satisfying the system of equations. In evaluating the summation in Equation (26), only those pairs of roots which have a small value of both P and u need to be considered.

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NOTATION

c = sorbate concentration in macropore
$C(t)$ = sorbate concentration in ambient solution
C_o, C_∞ = initial and final values of C
D_c = diffusivity in micropore (zeolite crystal)
D_p = macropore diffusivity (free area basis)
K = dimensionless equilibrium constant (crystal basis)
m_t = mass of sorbate adsorbed or desorbed during time t
m_∞ = mass of sorbate adsorbed or desorbed with $t \to \infty$
q = sorbate concentration at a point in the micropore (zeolite crystal)
$\bar{q}$ = sorbate concentration averaged over a microsphere
q_∞ = sorbate concentration in equilibrium with fluid concentration C_∞
r = radial coordinate for microsphere
r_c = radius of microsphere
R = radial coordinate for macrosphere
R_p = macroparticle radius
t = time
ϵ = macroporosity

Dimensionless Variables and Parameters

$\zeta = r/r_c$
$\eta = R/R_p$
$\tau = D_c t/r_c^2$
$N_c = \zeta q/q_\infty$
$N_p = \eta c/C_o$
$\beta = 3\alpha(1-\epsilon)q_\infty/\epsilon C_o$
$\Lambda = 1 - C_\infty/C_o$
$\alpha = (D_c/r_c^2)/(D_p/R_p^2)$
$\gamma = \beta\Lambda/[\beta + 3\alpha(1-\Lambda)]$

Laplace transform is defined as $L[X(t)] \equiv \tilde{X} \equiv \int_0^\infty e^{-st}X(t)\cdot dt$ with $p^2 = -s$.

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