Importance of intraparticle convection in the performance of chromatographic processes

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ABSTRACT

Large-pore materials are used in separation engineering as high-performance liquid chromatographic packings and adsorbents; however, they find also many applications in reaction engineering as catalyst supports and ceramic membrane reactors and in biotechnology as supports for mammalian cell cultures or biomass growth. In these large-pore materials, mass transport by intraparticle forced convection should be considered in process analysis. A brief historical survey of research work concerned with intraparticle forced convection is given, showing that the concept to be retained is that of effective diffusivity augmented by convection. The behaviour of the height equivalent to a theoretical plate as a function of bed superficial velocity is explained on the basis of the above concept. Analogies between slab and spherical particle geometries are discussed.

INTRODUCTION

Large-pore materials (*i.e.*, with pores larger than 1000 Å, as shown in Fig. 1) are used in several chemical engineering areas, namely as catalyst supports for selective oxidations [1,2], steam reforming, ammonia synthesis [3,4], etc., as adsorbents for the removal of carbonyl disulphide from propylene [5] or chromatographic supports, as high-performance liquid chromatographic (HPLC) packings based on alumina [6], polystyrene [7,8] or silica gel [9] for protein separations, as ceramic membranes [10], as supports for mammalian cell culture [11,12] and biomass growth [13] and in gel permeation chromatography [14].

The importance of intraparticle forced convection flow in large-pore or "gigaporous" materials (following Horváth's nomenclature [15]) was first discussed, as far as we could trace back, by Wheeler [16] in his landmark paper on "reaction rates and selectivity in catalyst pores". He concluded that intraparticle convective flow "is negligible except in the case of high-pressure reactions on catalysts with very large pores". He also wrote the mass balance equation for a species in a pore when diffusion, convection and reaction compete at the steady state.

The parameter relating intraparticle convective flow and diffusive flow (although not in dimensionless form) was denoted b. However, he did not solve the model equation and so he missed the point, later
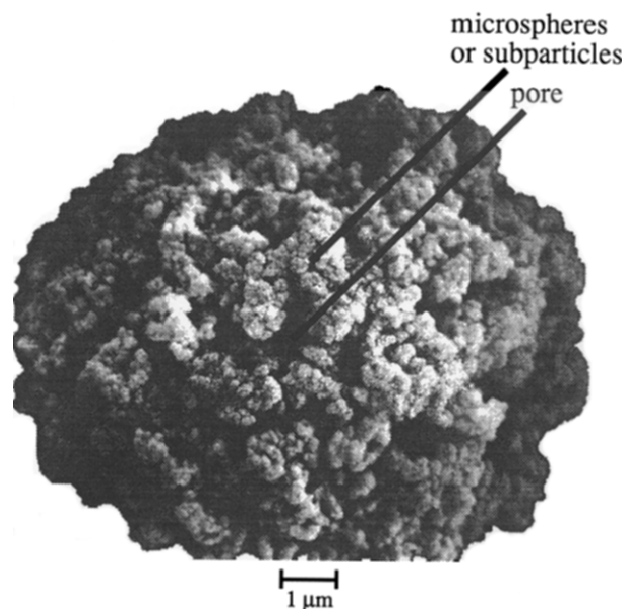

Fig. 1. Illustration of a large-pore material.

recognized by Nir and Pismen [17], that in the intermediate range of Thiele modulus the catalyst effectiveness factor was enhanced by intraparticle convection.

The need for large pores in catalyst preparation was recognized by Nielsen *et al.* [3] and Harbord [4], among others. Nielsen *et al.* claimed that "it would be appropriate if ... the catalyst in addition to the said micropores would have a system of coarse pores adapted to serve as ways of admission to the micropores".

In recent years, the use of large-pore supports in HPLC provided an extended area of application of the concept which is responsible for the enhanced performance observed with such supports. The concept can be presented as diffusivity augmented by convection, as shown in 1982 by Rodrigues *et al.* [2].

This paper has the following objectives: (i) to provide a historical survey of the use of large-pore supports in chemical engineering; (ii) to show that the concept behind the observed improvement in the performance of chromatographic processes is the diffusivity augmented by convection in large-pore supports; (iii) to draw analogies between slab and spherical geometries; and (iv) to discuss the behaviour of the height equivalent to a theoretical plate (HETP) as a function of superficial velocity.

CONCEPT OF DIFFUSIVITY AUGMENTED BY CONVECTION INSIDE PORES

Intraparticle mass transport includes, in general, flux contributions due to diffusion (Knudsen and continuum or ordinary diffusion), N_i^d, intraparticle forced convection (viscous or Poiseuille flow), N_i^v, and surface diffusion, N_i^s [18], as shown in Fig. 2. The total flux of species i is then

$$N_{i,\text{total}} = N_i^d + N_i^v + N_i^s \tag{1}$$

In the following we shall restrict the analysis to diffusive and viscous flow inside large-pore materials.

Let us consider mass transport of an inert or passive species inside a large-pore particle with slab geometry. The transient mass balance for species i is

$$D_e \cdot \frac{\partial^2 c_i'}{\partial z'^2} - v_0 \cdot \frac{\partial c_i'}{\partial z'} = \varepsilon_p \cdot \frac{\partial c_i'}{\partial t} \tag{2}$$
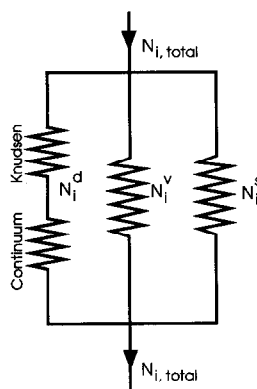

Fig. 2. Flux contributions of diffusion, convection and surface diffusion to the total flux.

where c_i' is the concentration of species i in the fluid phase inside the pores, z' is the particle space coordinate, t is the time variable, ε_p is the intraparticle porosity (pore volume/particle volume), v_0 is the intraparticle convective velocity and D_e is the effective diffusivity.

Introducing the dimensionless space variable $x = z'/l$ (l = half-thickness of the slab) and time constants for diffusion $\tau_d = \varepsilon_p l^2/D_e$ and convection $\tau_c = \varepsilon_p l/v_0$, we obtain

$$\frac{\partial^2 c_i'}{\partial x^2} - \frac{\tau_d}{\tau_c} \cdot \frac{\partial c_i'}{\partial x} = \tau_d \cdot \frac{\partial c_i'}{\partial t} \tag{2a}$$

The important parameter relating intraparticle convective flow and diffusive flow is the intraparticle Peclet number:

$$\lambda = \frac{\tau_d}{\tau_c} = \frac{v_0 l}{D_e} \tag{3}$$

introduced by Nir and Pismen [17] and closely related to the parameter b of Wheeler [16].

The transfer function of the particle system relating the Laplace transforms of the average tracer concentration inside the particle and the surface concentration is

$$g_p(s) = \frac{(e^{2r_2} - 1)(e^{2r_1} - 1)}{e^{2r_2} - e^{2r_1}} \frac{\sqrt{\lambda^2/4 + \tau_d s}}{\tau_d s} \tag{4}$$

where $r_1, r_2 = \lambda/2 \pm \sqrt{\lambda^2/4 + \tau_d s}$.

The classic analysis which considers only an "apparent" effective diffusivity, $\tilde{D}_e$, combines diffu-

sion and convection of the inert tracer; therefore, the unsteady-state mass balance equation is

$$\tilde{D}_e \cdot \frac{\partial^2 c_i'}{\partial z'^2} = \varepsilon_p \cdot \frac{\partial c_i'}{\partial t} \tag{5}$$

or

$$\frac{\partial^2 c_i'}{\partial x^2} = \tilde{\tau}_d \cdot \frac{\partial c_i'}{\partial t} \tag{5a}$$

with $\tilde{\tau}_d = \varepsilon_p l^2 / \tilde{D}_e$. The transfer function is now

$$\tilde{g}_p(s) = \frac{\tanh \sqrt{\tilde{\tau}_d s}}{\sqrt{\tilde{\tau}_d s}} \tag{6}$$

Model equivalence between moments of eqns. 4 and 6 leads to

$$\tilde{\tau}_d = \tau_d f(\lambda) \tag{7}$$

or

$$\tilde{D}_e = \frac{D_e}{f(\lambda)} \tag{8}$$

where $\tilde{D}_e$ is the "apparent" or "augmented" effective diffusivity due to convection and

$$f(\lambda) = \frac{3}{\lambda} \left(\frac{1}{\tanh \lambda} - \frac{1}{\lambda} \right)$$

The enhancement of the effective diffusivity, D_e by convection is

$$\frac{1}{f(\lambda)} = \frac{1}{\dfrac{3}{\lambda} \left(\dfrac{1}{\tanh \lambda} - \dfrac{1}{\lambda} \right)} \tag{9}$$

as shown in Fig. 3.

Eqn. 8 provides a tool for calculating the augmented effective diffusivity for any set of operating conditions. When intraparticle convective flow is negligible ($\lambda \ll 1$), $\tilde{D}_e = D_e$; at high λ, however, the enhancement of the effective diffusivity is $\tilde{D}_e/D_e = \lambda/3$ and so $\tilde{D}_e = v_0 l/3$.

This result should be compared with those in other works. Van Kreveld and Van den Hoed [19] suggested that intraparticle convection could be important and used an augmented diffusivity containing a term proportional to the bed superficial velocity u_0, i.e., $\tilde{D}_e = D + u_0 D'$. In the limit of strong convection $\tilde{D}_e = u_0 D'$. Later, Afeyan et al. [7], following this idea, used $\tilde{D}_e \approx v_0 d_p/2$ "based on the assumption that the concentration terms governing
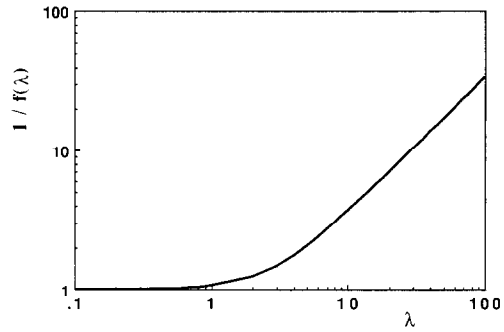

Fig. 3. Enhancement of effective diffusivity by convection $1/f(\lambda)$ as a function of the intraparticle Peclet number λ.

diffusion and convection can be treated as approximately equal". If we try to make an analogy with slab geometry where $\tilde{D}_e \approx v_0 l/3$, we shall obtain $l = 3 d_p/2$, which does not make sense. This calls for a closer examination of the analogy between slab and spherical geometries.

ANALOGY BETWEEN SLAB AND SPHERICAL GEOMETRIES

In catalytic reaction engineering, analogies between various particle shapes can be made by introducing a characteristic dimension V_p/A_p (ratio of particle volume and external area). For slabs this dimension is the half-thickness l, for spheres it is $R_p/3$, where R_p is the particle radius, and for infinite cylinders it is $R_p/2$.

The equivalence for steady-state reaction/diffusion problems between slab and spherical catalysts is then based on

$$l_{slab} = R_{p,sphere}/3 \tag{10a}$$

However, for transient diffusion the equivalence should be based on the equality of the diffusion time constants for slabs and spheres, i.e., [20]

$$\tau_{d,slab} = \frac{\varepsilon_p l^2}{D_e} \quad \text{and} \quad \tau_{d,sphere} = \frac{\varepsilon_p R_p^2}{5 D_e}$$

where the diffusion time constant for sphere results from the linear driving force approximation. The result is

$$l_{slab} = R_{p,sphere}/\sqrt{5} \quad \text{(transient diffusion)} \tag{10b}$$

Similarly for fully convective flow ($\lambda \gg 1$), the equivalence between slab and sphere should be based on the equality of the time constants for intraparticle convection, *i.e.*,

$$\tau_{c,slab} = 2\,l/v_0 \quad \text{and} \quad \tau_{c,sphere} = \langle l_c \rangle / v_0$$

It can be shown [21] that the average convective path for a sphere is $\langle l_c \rangle = 4\,R_p/3$. Hence the equivalence leads to

$$l_{slab} = R_{p,sphere}/1.5 \quad \text{(transient convection)} \quad (10c)$$

INTRAPARTICLE CONVECTIVE VELOCITY, v_0

The intraparticle convective velocity, v_0, is calculated from Darcy's law:

$$v_0 = -\frac{B_p}{\mu} \cdot \frac{\Delta p}{2l} \quad (11)$$

where

$$B_p = \frac{\varepsilon_p^3}{150(1 - \varepsilon_p)^2} \cdot d_m^2 = \frac{a\varepsilon_p^3}{150(1 - \varepsilon_p)^2} \cdot d_{pore}^2$$

is the particle permeability, d_m is the diameter of the microspheres inside the particle, d_{pore} is the pore diameter, $a = d_m^2/d_{pore}^2$ is a constant ($a = 4$ for POROS according to Afeyan *et al.* [7]), ε_p is the intraparticle porosity, μ is the fluid viscosity and $\Delta p/2l$ is the pressure drop across a particle with thickness $2l$.

Komiyama and Inoue [22], in a pioneer (and also forgotten) paper, and later Rodrigues *et al.* [2] used, as a first approximation for calculating the intraparticle convective velocity v_0, the equality between $\Delta p/2l$ and the pressure drop along the bed of length L, $\Delta P/L$, given by Ergun's law, *i.e.*,

$$\frac{\Delta p}{2l} = \frac{\Delta P}{L} \quad (12)$$

After correction to refer fluxes to the same area, we obtain a relationship between v_0 and the bed superficial velocity u_0. Generally the relationship is $v_0 = a_1 u_0 + a_2 u_0^2$. In the case of laminar flow through the bed, the relationship is simply $v_0 = a_1 u_0$, where

$$a_1 = \frac{B_p}{B_b} \cdot \frac{1 - \varepsilon_b}{\varepsilon_p} \quad (13)$$

$$B_b = \frac{\varepsilon_b^3}{150(1 - \varepsilon_b)^2} \cdot d_p^2$$

is the bed permeability, ε_b is the interparticle bed porosity and d_p is the particle diameter.

An order of magnitude analysis carried out by Afeyan *et al.* [7] showed that the intraparticle Peclet number in HPLC operations can be as high as 60.

EFFECT OF INTRAPARTICLE CONVECTION ON HETP

HETP is often used as a measure of the performance of chromatographic processes. The Van Deemter equation [23] describes how the HETP changes with the bed superficial velocity u_0. For a fixed-bed chromatographic process including axial dispersion, intraparticle diffusion and convection and based on linear adsorption equilibrium between mobile and stationary phases $q_i^* = m\,c_i'$, the model equations are as follows.

The mass balance for species i in the fluid phase is

$$\varepsilon_b D_{ax} \cdot \frac{\partial^2 c_i}{\partial z^2} - u_0 \cdot \frac{\partial c_i}{\partial z} - \left[\varepsilon_b \cdot \frac{\partial c_i}{\partial t} + b\varepsilon_p(1 - \varepsilon_b) \frac{\partial \langle c_i' \rangle}{\partial t} \right] = 0 \quad (14)$$

where c_i is the concentration of species i in the fluid phase outside the particles, z is the bed axial coordinate, u_0 is the bed superficial velocity (flow-rate/bed cross-sectional area $= U/A$), $\langle c_i' \rangle$ is the average concentration of species i in the fluid phase inside the particles and

$$b = 1 + \frac{1 - \varepsilon_p}{\varepsilon_p} m = 1 + k^*$$

(k^* is the capacity ratio for the particle). In dimensionless form, the mass balance is

$$\frac{1}{Pe} \cdot \frac{\partial^2 c_i}{\partial \zeta^2} - \frac{\partial c_i}{\partial \zeta} - \left[\varepsilon_b \cdot \frac{\partial c_i}{\partial \theta} + b\varepsilon_p(1 - \varepsilon_b) \frac{\partial \langle c_i' \rangle}{\partial \theta} \right] = 0 \quad (14a)$$

where $Pe = u_0 L/(\varepsilon_b D_{ax})$ is the Peclet number, $\zeta = z/L$ is the dimensionless bed axial coordinate, $\theta = t/\tau = t\,u_0/L$ is the dimensionless time and L is the bed length.

Boundary and initial conditions for eqn. 14a are $\zeta = 0$, $c_i = M\,\delta(\theta)$; $\zeta \to \infty$, c_i limited and $\theta = 0$, $c_i = 0$, $\forall \zeta$.

The mass balance for species i inside the particle in dimensionless form is

$$\frac{\partial^2 c_i'}{\partial x^2} - \lambda \cdot \frac{\partial c_i'}{\partial x} = b\alpha \cdot \frac{\partial c_i'}{\partial \theta} \tag{15}$$

where $\alpha = \tau_d/\tau$, with boundary and initial conditions $x = 0$ and $x = 2$, $c_i' = c_{is}'$ and at $\theta = 0$, $c_i' = 0$, $\forall x$.

The transfer function of the system relating the outlet concentration and the inlet concentration in the Laplace domain is

$$G(s) = \exp\left[\frac{Pe}{2} - \sqrt{\frac{Pe^2}{4} + PeN(s)}\right] \tag{16}$$

with

$$N(s) = \varepsilon_b s + b\varepsilon_p(1 - \varepsilon_b)sg_p(s) \tag{16a}$$

where $g_p(s)$ is given by eqn. 4 after replacing $\tau_d s$ by $b\alpha s$, to account for the Laplace transform relative to the reduced time θ instead of the real time t and for the linear adsorption of species i inside the particle.

The moments of the impulse response are

$$\mu_1 = \varepsilon_b + \varepsilon_p(1 - \varepsilon_b)b \tag{17a}$$

$$\mu_2 = \frac{2}{3}\varepsilon_p(1 - \varepsilon_b)b^2\alpha\,f(\lambda) +$$

$$\left(1 + \frac{2}{Pe}\right)[\varepsilon_b + \varepsilon_p(1 - \varepsilon_b)b]^2 \tag{17b}$$

and so the variance is

$$\sigma^2 = \frac{2}{Pe} \cdot \mu_1^2 + \frac{2}{3}\varepsilon_p(1 - \varepsilon_b)b^2\alpha\,f(\lambda) \tag{17c}$$

The HETP defined as $\sigma^2 L/\mu_1^2$ is then

$$HETP = \frac{2L}{Pe} + \frac{2}{3} \cdot \frac{\varepsilon_p(1 - \varepsilon_b)b^2\alpha L}{[\varepsilon_b + \varepsilon_p(1 - \varepsilon_b)b]^2} \cdot f(\lambda) \tag{18}$$

or

$$HETP = A + \frac{B}{u_0} + Cu_0 \tag{19}$$

In the classical analysis by Van Deemter et al. [23], where intraparticle forced convection is not considered, $f(\lambda) = 1$ and so

$$C = \frac{2}{3} \cdot \frac{\varepsilon_p(1 - \varepsilon_b)b^2}{[\varepsilon_b + \varepsilon_p(1 - \varepsilon_b)b]^2} \cdot \boxed{\tau_d} \tag{20}$$

Here this coefficient is modified to account for the

augmented effective diffusivity [24], i.e., τ_d is replaced by $\tau_d f(\lambda)$ as shown in eqn. 7, i.e.,

$$C = \frac{2}{3} \cdot \frac{\varepsilon_p(1 - \varepsilon_b)b^2}{[\varepsilon_b + \varepsilon_p(1 - \varepsilon_b)b]^2} \cdot \boxed{\tau_d f(\lambda)} \tag{21}$$

At high λ ($\lambda \gg 1$), we have $\tau_d f(\lambda) = 3\,l\,\varepsilon_p/v_0$ and so the limiting value of the HETP, neglecting the contribution of dispersion, is given by

$$HETP \approx \frac{2\varepsilon_p^2(1 - \varepsilon_b)b^2}{[\varepsilon_b + \varepsilon_p(1 - \varepsilon_b)b]^2} \cdot \frac{l}{v_0} \cdot u_0 \tag{22}$$

As $v_0 = a_1 u_0$ with a_1 given by eqn. 13, we obtain

$$HETP \approx \frac{2\varepsilon_p^2(1 - \varepsilon_b)b^2 l}{a_1[\varepsilon_b + \varepsilon_p(1 - \varepsilon_b)b]^2} \tag{22a}$$

For highly adsorbed solutes, $b \gg 1$, we have

$$HETP \approx \frac{2l}{(1 - \varepsilon_b)a_1} \tag{23}$$

Fig. 4 shows HETP as a function of the bed superficial velocity for conventional supports and large-pore supports. Using the data of Afeyan et al. [7], $d_p = 10\ \mu m$, $d_{pore} = 7000\ \text{Å}$, $\varepsilon_p = 0.5$, $\varepsilon_b = 0.35$, we obtain $B_b = \varepsilon_b^3 d_p^2/[150\ (1 - \varepsilon_b)^2] \approx 6.8 \cdot 10^{-10}\ cm^2$, $B_p = 4\varepsilon_p^3 d_{pore}^2/[150\ (1 - \varepsilon_p)^2] \approx 6.5 \cdot 10^{-11}\ cm^2$ and $a_1 = B_p(1 - \varepsilon_b)/(B_b\varepsilon_p) \approx 0.126$, which means that the intraparticle convective velocity is around 4.5% of the bed interstitial velocity, and so for highly adsorbed solutes HETP $\approx 8\ d_p$ according to eqn. 23. For non-retained species $b = 1$ and from eqn. 22a we obtain HETP $\approx 2\ d_p$.

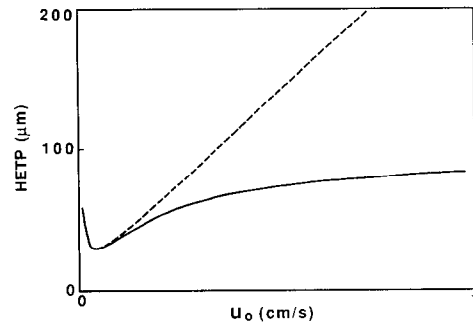Fig. 5 shows the upper limit of the reduced HETP,

Fig. 4. HETP as a function of the bed superficial velocity u_0. Dashed line, Van Deemter equation for conventional supports; solid line, extension of Van Deemter equation to large-pore supports.
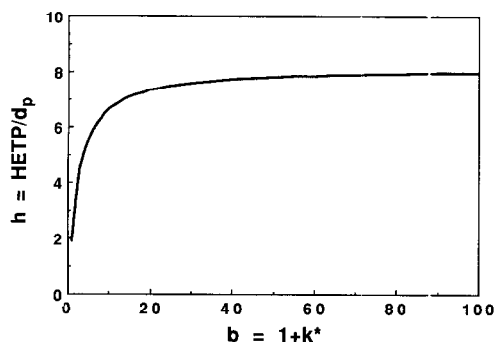
Fig. 5. Reduced HETP (h = HETP/d_p) as a function of the parameter b = 1 + k^*.

Fig. 7. Breakthrough curves $F(\theta)$ = c_{out}/c_{feed} as a function of reduced time. Dashed line, u_0 = 0.282 cm/s, no convection (λ = 0); solid line, with intraparticle convection, u_0 = 0.282, 0.576 and 0.963 cm/s.

h (= HETP/d_p), for high λ as a function of the parameter b = 1 + k^*.

The response of the chromatographic column to an impulse of inert tracer can be obtained by inversion of the bed transfer function, eqn. 16, *i.e.*, $E(\theta)$ = $\mathscr{L}^{-1}[G(s)]$. Fig. 6 shows $E(\theta)$ as a function of the reduced time θ for conventional supports (λ = 0) and for a large-pore support (λ = 35.5). It can be seen that intraparticle convection sharpens the peak and so leads to a lower HETP.

Fig. 7 shows the breakthrough curves, *i.e.*, bed responses to step changes in feed concentration, $F(\theta)$ = c_{out}/c_{feed}, for conventional supports (λ = 0) and large-pore supports, where intraparticle convection is important. In this instance the curves were calculated at three different superficial velocities and were identical, showing that velocity has no influence on the breakthrough curves. This is equivalent
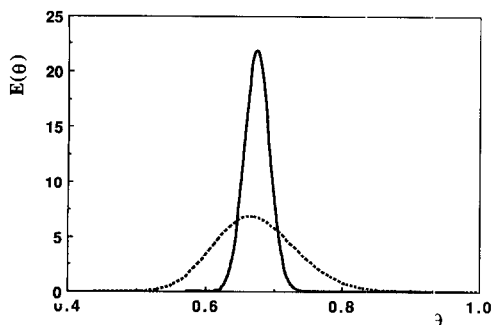
to the plateau in HETP *versus* u_0 curve shown in Fig. 4.

CONCLUSIONS

The improvement of the performance of chromatographic processes using large-pore supports is due to the effective diffusivity augmented by convection. A complete relationship between the augmented diffusivity and the intraparticle Peclet number is available for slab geometry. Analogies between slab and sphere can be drawn in limiting cases.

It is interesting that some large-pore catalysts compete with shell-type catalysts, *e.g.*, in ethylene oxidation; in HPLC there is also a choice between pellicular and flow-through particles.

In HPLC, increasing the bed superficial velocity will lead to a limiting value of HETP which is proportional to the particle diameter and depends on the bed and particle permeabilities. The performance of a chromatographic column containing a large-pore packing is better than that with conventional supports, as the HETP is lower; moreover, increasing u_0 does not lead to a significant decrease in column efficiency and so one can speed up the separation. Along HETP *versus* u_0 curves the intraparticle Peclet number is changing. However, in gas–solid chromatography the relationship between the intraparticle convective velocity v_0 and the bed superficial velocity u_0 is v_0 = $a_1 u_0$ + $a_2 u_0^2$ (assuming Ergun's law for the bed pressure drop); as a consequence, HETP will pass through a maximum

Fig. 6. Impulse response of the HPLC column to an inert tracer as a function of reduced time (u_0 = 0.282 cm/s; α = 0.0157). Dashed line, no intraparticle forced convection (λ = 0); solid line, λ = 35.5.
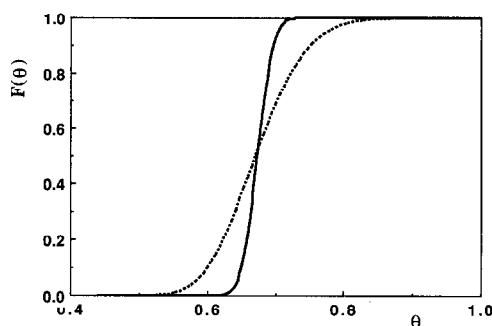
before it reaches a plateau at a high bed superficial velocity [24].

In this work the kinetics of adsorption/desorption on the stationary phase were assumed to be infinitely fast, so the results presented here correspond to the more favourable situation; nevertheless, they are supported by experimental observations [7,8,15,20]. This assumption is not always valid. Slow kinetics will contribute with an extra term for HETP in the Van Deemter equation, proportional to u_0, i.e., $D u_0$. However, the HETP for large-pore packings will be always lower than the corresponding HETP obtained with conventional supports [25].

ACKNOWLEDGEMENTS

SYMBOLS

b	parameter ($= k^* + 1$)
B_b	bed permeability, m^2
B_p	particle permeability, m^2
c_i	species concentration in the external fluid phase, kmol/m^3
c_i'	species concentration in the fluid phase inside the particle, kmol/m^3
d_m	diameter of microspheres inside the particle, m
d_p	particle diameter, m
d_{pore}	pore diameter, m
D_e	effective diffusivity, m^2/s
$\tilde{D}_e$	augmented effective diffusivity, m^2/s
$E(\theta)$	impulse response of the bed
$F(\theta)$	response of the bed to a step input of concentration
h	reduced HETP ($=$ HETP/d_p)
HETP	height equivalent to a theoretical plate, m
k^*	particle capacity factor
l	half thickness of the slab, m
L	bed length, m
m	slope of the adsorption equilibrium isotherm
Pe	Peclet number
Δp	pressure drop across the particle, Pa
ΔP	bed pressure drop, Pa
q_i^*	adsorbed phase concentration in equilibrium with c_i', kmol/m^3 of solid
R_p	particle radius, m

s	Laplace variable
t	time, s
u_0	bed superficial velocity, m/s
v_0	intraparticle convective velocity, m/s
x	reduced space coordinate for the particle ($= z'/l$)
z	axial coordinate for the bed, m
z'	axial coordinate for the particle, m

Greek symbols

α	ratio of time constant for diffusion and space time ($= \tau_d/\tau$)
ε_b	bed porosity (interparticle volume/bed volume)
ε_p	intraparticle porosity (pore volume/particle volume)
λ	intraparticle Peclet number
μ	fluid viscosity, kg/m · s
μ_i	moments of ith order of the impulse response
θ	reduced time ($= t/\tau$)
σ^2	variance
τ	space time ($= L/u_0$), s
τ_c	time constant for intraparticle convection, s
τ_d	time constant for intraparticle diffusion, s
$\tilde{\tau}_d$	"apparent" time constant for intraparticle diffusion, s
ζ	reduced axial coordinate for the bed ($= z/L$)

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