Diffusion time in core–shell packing materials

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ABSTRACT

The recently developed pellicular packing materials show high efficiency and have attracted great interest. The improved mass-transfer kinetics of the core–shell particles is due to the shorter diffusion path of the molecules within the stationarity phase. In this study we show how the diffusion time of the molecules visiting the stationary phase depends on the geometry of the porous shell stationary phase. The mean escape time of diffusion is calculated on the basis of a random walk model.

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1. Introduction

The recent introduction of novel core–shell packing materials has evoked a renewed interest in the comparison of the mass-transfer properties of fully porous and porous layer packing materials.

The outstanding separation performance of the shell-type particles has been demonstrated in a large number of experimental and theoretical studies [1–5]. The results of all those studies agree that the number of theoretical plates one can achieve using 2.7-μm or 2.6-μm shell particles is equivalent to that of sub-2-μm fully porous particles.

The real advantage of the shell-type particles is observed for the separation of large molecules, during the separation of which the intraparticle diffusion is the dominating contribution to the total plate height [2,6,7]. Horváth et al. investigated the influence of the thickness of the porous shell on the peak resolution and determined that the maximum increase of resolution can be achieved when the porous shell is so thin that the loadability of the column may seriously be affected [7].

In the present study, we will introduce a method to calculate the mean diffusion time within porous and shell-type stationary phases of various porous shell thickness. A one-dimensional random walk of a single molecule is considered to build the model, which is then extended to spherical particles and cylindrical monolith structures. This concept confirms the advantage of shell particles with thin porous shells.

Intraparticle diffusion and other details of the chromatographic process, such as mobile phase axial dispersion, external mass transfer, and the kinetics of adsorption–desorption process are usually described with the plate height equation derived from the general rate model of chromatography [8–11]. The moments calculated from the general rate model allow the derivation of a detailed plate height equation for both particulate and monolithic columns [12] as well as for core–shell particles [2].

The microscopic – statistical, or stochastic – concepts that are employed in this study envision the chromatographic processes at a molecular level via the random migration of the molecules.

There have been a number of attempts to compare the microscopic and the macroscopic models of chromatography. The simplest approach is to compare the first and the second moments of the band profiles [13], but it has been demonstrated that not only the first and the second moments but also the whole peak shape obtained with the stochastic–dispersive and with the lumped kinetic models are identical [14].

2. Theory

We assume that on a one-dimensional grid a particle steps at discrete times with constant-length steps. Then we calculate the mean time the molecule has to randomly wander to a given position. Afterwards, the one-dimensional model is extended to spherical or cylindrical geometries. The problem we want to answer is the following: when a molecule is found at a random position in the stationary phase, how long does it take to escape by diffusion to the interstitial zone of the column?

2.1. Mean time to escape in one dimension

First we start with a one-dimensional diffusion problem [15]. We release a molecule at position x at time $t = 0$. The randomly diffusing molecule jumps to the left or to the right a distance δ every τ_0 second. Therefore, at time $t = \tau_0$, the molecule will be either at position $x - \delta$ or $x + \delta$ with equal probabilities of 1/2. The mean time

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to escape from those positions are $\hat{t}(x - \delta)$ or $\hat{t}(x + \delta)$, respectively. The average for $\hat{t}(x)$ is

$$\hat{t}(x) = \tau_0 + \frac{1}{2}[\hat{t}(x + \delta) + \hat{t}(x - \delta)] \tag{1}$$

The above equation can simply be rearranged into

$$\frac{1}{\delta}[\hat{t}(x + \delta) - \hat{t}(x)] - \frac{1}{\delta}[\hat{t}(x) - \hat{t}(x - \delta)] + \frac{2\tau_0}{\delta} = 0 \tag{2}$$

When δ is very small, we can write differentials instead of the differences in the above equation and obtain:

$$\frac{d\hat{t}}{dx}\bigg|_x - \frac{d\hat{t}}{dx}\bigg|_{x-\delta} + \frac{2\tau_0}{\delta} = 0 \tag{3}$$

When we divide the above equation by δ, exploit that the diffusion coefficient is $D = \delta^2/2\tau_0$, and once again we assume that δ is very small so that differentials can be written instead of the differences, we obtain the following differential equation:

$$\frac{d^2\hat{t}}{dx^2} + \frac{1}{D} = 0 \tag{4}$$

This differential equation should be solved with the proper boundary conditions in order to calculate the mean time a molecule needs to wander before it arrives to a determined position. In the followings, this differential equation will be considered in various three-dimensional environments, and in this manner we will calculate the average time a diffusion takes before the molecule leaves the porous particle.

In a two- or three-dimensional system, the diffusion coefficient can be defined by the Einstein–Smoluchowski equation as $D = \delta^2/4\tau_0$ and $D = \delta^2/6\tau_0$, respectively. Therefore, the differential equation for the diffusion time in two or three dimensions is

$$\nabla^2\hat{t} + \frac{1}{D} = 0 \tag{5}$$

where ∇^2 is the two- or three-dimensional Laplacian.

3. Results and discussion

3.1. Diffusion time in porous and in shell-type particles

For three-dimensional diffusion and for spherical particles, Eq. (5) can be written as

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\hat{t}}{dr}\right) + \frac{1}{D_p} = 0 \tag{6}$$

For a porous particle of radius r_p, we can write the following boundary conditions. When a molecule is at the surface of the particle, at $r = r_p$, the mean time to escape is zero. Furthermore, the mean time to escape has a maximum at the center of the particle and at $r = 0$ we have $d\hat{t}/dr = 0$. Thus, Eq. (6) is solved with the following boundary conditions

$$\hat{t}(r = r_p) = 0 \quad \text{and} \quad \frac{d\hat{t}}{dr}\bigg|_{r=0} = 0 \tag{7}$$

The solution gives the mean time to escape from position r in a porous particle

$$\hat{t}(r) = \frac{r_p^2 - r^2}{6D_p} \tag{8}$$

When molecules are uniformly distributed within the spherical particle, the average value of the mean time to escape is obtained as

$$\tau = \frac{\int_0^{r_p} 4\pi r^2 \hat{t}(r)dr}{\int_0^{r_p} 4\pi r^2 dr} = \frac{r_p^2}{15D_p} \tag{9}$$
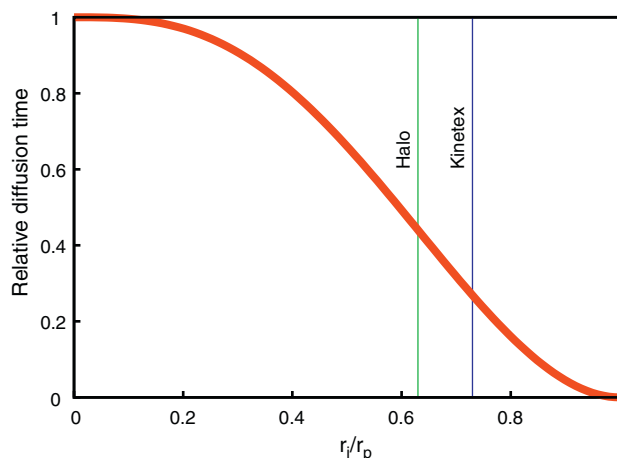

Fig. 1. Relative diffusion time against the ratio of the solid core and the total particle size.

This diffusion time is the reciprocal of the intraparticle rate constant term of the plate height equation calculated from the general rate model. Thus a direct connection is made between the general rate model and the microscopic random walk model.

When the particle is not fully porous but the center of the particle is composed of a fluidimpervious solid core of radius r_i, the boundary conditions will change to

$$\hat{t}(r = r_p) = 0 \quad \text{and} \quad \frac{d\hat{t}}{dr}\bigg|_{r=r_i} = 0 \tag{10}$$

Eq. (6) is solved with these boundary conditions and the mean time to escape from position r in a core–shell particle is obtained as

$$\hat{t}(r) = \frac{(r_p - r)(r^2 + r_p r - 2q^3 r_p^2)}{6D_p r} \tag{11}$$

where $q = r_i/r_p$ is the relative size of the solid core. When molecules are uniformly distributed within the core–shell particle, the average value of the mean time to escape is obtained as

$$\tau = \frac{\int_{r_i}^{r_p} 4\pi r^2 \hat{t}(r)dr}{\int_{r_i}^{r_p} 4\pi r^2 dr} = \frac{r_p^2}{15D_p}\frac{(1 - q)^2[1 + q(3 + q(6 + 5q))]}{1 + q + q^2} \tag{12}$$

A comparison of Eqs. (9) and (12) shows the advantage of shell particles to fully porous ones as far as the intraparticle diffusion is concerned. Fig. 1 illustrates the decrease of diffusion time in core–shell particles relative to that in fully porous particles. When the diameter of the solid core is less than 40% of the total diameter, the relative decrease of the diffusion time is less than 20%. Although the diffusion path is shorter, the geometry does not favor diffusion, since the solid core presents a reflecting boundary. Any further increase of the relative size of the solid core, however, will strongly reduce the diffusion time.

For a Halo or a Poroshell 120 particle $q = 1.7/2.7 = 0.63$. From that value we get that in a Halo particle, the mean diffusion time of a molecule for a single visit should be 44% of the one in a fully porous particle of the same diameter. For a Kinetex particle $q = 1.9/2.6 = 0.73$, therefore in a Kinetex particle, the diffusion time should only be 27% of the diffusion time in a same-diameter fully porous particle.

The plate-height equation for core–shell particles was derived by Gengliang and Zhide [16] and by Kaczmarski and Guiochon [2] using the general rate model of chromatography. In that model, an external mass-transfer coefficient expresses the fluid-to-particle resistance, and the mass-transfer resistance that is due to the slow

diffusion in the pores is described by an internal mass-transfer coefficient. The overall mass-transfer coefficient k is calculated from the external (k_{ext}) and internal (k_{int}) mass-transfer coefficients:

$$\frac{1}{k} = \frac{1}{k_{ext}} + \frac{1}{k_{int}} \tag{13}$$

Kaczmarski and Guiochon obtained the internal mass transfer coefficient for core–shell particles in the following form (Eq. (30) of Ref. [2]):

$$\frac{1}{k_{int}} = \frac{r_p}{5D_p} \frac{(1-q)[1+q(3+q(6+5q))]}{(1+q+q^2)^2} \tag{14}$$

A first-order rate constant may be calculated from the internal mass-transfer coefficient:

$$k'' = \frac{3k_{int}}{r_p} \tag{15}$$

where $r_p/3$ is the volume-to-surface ratio of a spherical particle. A comparison of Eq. (12) with Eqs. (14) and (15) gives

$$\tau = \frac{1}{k''}(1-q^3) \tag{16}$$

Therefore we can conclude that the mean diffusion time – obtained from a random walk model – and the rate constant for internal mass transfer – obtained from the moments of the general rate model – are equivalent since $1-q^3$ is merely a scaling factor: the volume fraction of the porous shell of a particle. That parameter has to be taken into account in the phase ratio.

3.2. Diffusion time in cylindrical and in porous-shell pillar stationary phase

The structure of the stationary phase in a monolithic chromatographic column is a solid composed of a thin, porous skeleton and large-diameter macropores. The generale rate model of monolithic columns was developed by Miyabe and Guiochon assuming that the structure of the monolith can be approximated by porous cylinders that contain the mesopores and are located in the center of cylindrical macropores [12].

We write Eq. (5) for cylindrical coordinates to obtain the mean diffusion time of a molecule within a monolithic structure.

$$\frac{1}{r}\frac{d\hat{t}}{dr} + \frac{d^2\hat{t}}{dr^2} + \frac{1}{D_p} = 0 \tag{17}$$

Using the above detailed strategy, we can calculate the diffusion time in a porous monolith with a radius of the cylindrical skeleton being r as

$$\tau = \frac{r^2}{8D_p} \tag{18}$$

This expression is identical to the reciprocal of the rate constant for internal mass transfer in monolithic columns [12].

De Malsche et al. suggested the use of porous shell pillar structures as the cylindrical equivalent of the porous shell particles [17]. Although that column technology seems to be dormant, the diffusion time in a porous shell cylinder reduces as the size of the solid core increases.

When we solve Eq. (17) for the boundary conditions of a porous shell cylindrical system, the following diffusion time is obtained:

$$\tau = \frac{r^2}{8D_p}\left[1 - 3q^2 + \frac{4q^4\ln q}{q^2-1}\right] \tag{19}$$

This diffusion time is equivalent to the reciprocal of the rate constant for internal mass transfer obtained for porous shell pillars by De Malsche et al. [17].

4. Conclusions

We used a microscopic random walk model of diffusion [15] to calculate the mean diffusion time in fully porous and shell-type packing materials. The calculations show that the relative decrease of the diffusion time is rather significant with the currently available core–shell packing materials. The diffusion times calculated on the basis of the microscopic random walk model are equivalent with the appropriate intraparticle mass-transfer kinetics terms.

As long as the diffusion time is considered, the 2.7-μm Halo and Poroshell 120 phases are equivalent to a 1.8-μm fully porous packing material. The 2.6-μm Kinetex packing material is equivalent to a 1.34-μm fully porous stationary phase.

Hindered diffusion – which is observed when the size of the analyte macromolecules becomes comparable to the pore diameter – affects both fully porous and core–shell packing materials in the same manner. It will, however, cause a much more momentous band broadening in fully porous particles where diffusion path as well as diffusion time are longer than in core–shell particles.

We should emphasize that here only the intraparticle diffusion has been considered; the effects of retention, external mass transfer, mobile phase dispersion, or extra-column instrumental broadening are not taken into account. Therefore the realistic advantage of the core–shell particles may be smaller than the numbers presented here would indicate it.

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