



Rationale behind the optimum efficiency of columns packed with new 1.9 μm fully porous particles of narrow particle size distribution



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ARTICLE INFO

Article history:

Received 6 March 2016

Received in revised form 7 May 2016

Accepted 10 May 2016

Available online 12 May 2016

Keywords:

Column efficiency

Sub-2 μm fully porous particles of narrow particle size distribution (nPSD)

Mass transfer

Eddy dispersion

ABSTRACT

Columns packed with new commercially available 1.9 fully porous particles of narrow particle size distribution (nPSD) are characterized by extremely high efficiency. Under typical reversed phase conditions, these columns are able to generate very high number of theoretical plates (in the order of 300,000 plates/m and more). In this paper, we investigate the origin of the high performance of these nPSD columns by performing a series of measurements that include, in addition to the traditional determination of the van Deemter curve, peak parking, pore blocking and inverse size exclusion experiments. Two nPSD columns (both 100×3.0 mm) have been considered in this study: the first one, packed with particles of 80 Å pore size, is commercially available. The second one is a prototype column packed with 1.9 fully porous particles of 120 Å pore size.

The main conclusion of our study is that these nPSD columns are characterized by extremely low eddy dispersion, while longitudinal diffusion and mass transfer kinetics are substantially equivalent to those of other fully porous particles of similar chemistry.

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1. Introduction

In the companion paper to this one [1], the kinetic performance of columns packed with the recently introduced 1.9 μm fully porous particles (average pore diameter 80 Å), known with the commercial name of Titan C₁₈, has been investigated by using a series of benzene derivatives under reversed phase (RP) conditions. The study was performed on a set of 6 columns (length: 50, 75 and 100 mm, internal diameter 2.1 and 3 mm) that represents, in our opinion, a large enough sample to draw reliable conclusions on their kinetic behaviour. The most relevant results from that study confirmed, on the one hand, the excellent kinetic performance of narrow particle size distribution (nPSD) columns already demonstrated in literature [2,3] (with reduced HETP, h , as small as 1.7–1.9) but, on the other hand, revealed how these columns can be very efficiently operated even at relatively large flow rates [1].

This latter conclusion thus contrasts those of Gritti and Guiochon [2,3] who observed, by using a series of phenone derivatives under RP conditions, a dramatic loss of performance when the column was operated at velocities slightly larger than the optimum. Gritti and Guiochon explained this finding on the base of the very low intraparticle diffusivity that would characterize the Titan C₁₈ particles (about three times smaller, for a retention factor of 2, than for typical fully porous C₁₈ particles). Following [2,3], the unusually low intraparticle diffusivity not only explains the very good performance of these columns at relatively low flow rates (thanks to very reduced longitudinal dispersion) but also their scarce performance at high flow rates due to slow mass transfer [2,3]. On the other hand, no effect on eddy dispersion was observed.

In the attempt of giving an explanation for the observed differences, in this study we present a detailed investigation of contributions to band broadening of the individual steps involved in the migration of the compound peaks through heterogeneous porous media. Essentially the same experimental protocol as in [2,3] was employed. It requires peak parking [4–7], total pore-blocking [8,9] and accurate HETP measurements. Combined with

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models of effective longitudinal diffusion through the packed bed [10–12], this information permits to achieve a physically-sound interpretation of mass transfer in modern liquid chromatography (LC) columns. The main study was performed by using a series of benzene derivatives as probe compounds, however, for the sake of comparison, the van Deemter curves of phenone derivatives used in [2,3] were also measured.

Finally, besides the Titan C₁₈ column packed with 1.9 μm fully porous particles with average pore size 80 Å used in previous works [1–3], a prototype column (supplied by Supelco) was also fully characterized from a kinetic viewpoint. This column is packed with Titan C₁₈ 1.9 μm but of average pore size 120 Å

2. Theory

Under the hypothesis of independence of the different contributions leading to peak broadening in LC [13,14], the functional relationship between the reduced plate height $h = H/d_p$ (being H the HETP and d_p the particle diameter) and the interstitial reduced velocity v is commonly written as the sum of three terms including the eddy dispersion, $a(v)$, the longitudinal diffusion, b/v , and the mass transfer resistance across the stationary phase, $c_s v$ [15,16], that is:

$$h = a(v) + \frac{b}{v} + c_s v \quad (1)$$

The interstitial reduced velocity is defined as:

$$v = \frac{u_e d_p}{D_m} \quad (2)$$

where D_m is the bulk molecular diffusion coefficient and u_e is the interstitial velocity, i.e. the velocity referred to the mobile phase moving between particles [17]:

$$u_e = \frac{F_v}{\pi r_c^2 \epsilon_e} \quad (3)$$

being F_v the flow rate, r_c the inner column radius and ϵ_e the external column porosity:

$$\epsilon_e = \frac{V_e}{V_{col}} \quad (4)$$

with V_{col} the geometric volume of the column.

For columns packed with very fine particles, usually a term accounting for the frictional heating due to the stream of the mobile phase against the bed under significant pressure must be added to Eq. (1). However, given the quasi-adiabatic conditions under which experiments were performed, it was not necessary to add this term [18–21].

The meaning of the different terms appearing in Eq. (1) is well known. The longitudinal (or axial) diffusion term describes the band broadening due to the diffusion of molecules through the porous particles and the interstitial volume in absence of flow. Since this is the only contribution to band broadening when the flow is switched off, it is best estimated through peak parking experiments [4–7]. In reduced coordinates, the longitudinal diffusion term b is given by [5,13,15,22]:

$$b = 2(1 + k_1) \frac{D_{eff}}{D_m} = 2(1 + k_1) \gamma_{eff} \quad (5)$$

where D_{eff} is the effective longitudinal diffusion coefficient, γ_{eff} ($= D_{eff}/D_m$) is the dimensionless effective diffusion coefficient and k_1 is the zone retention factor, defined as [5,23]:

$$k_1 = \frac{t_R - t_e}{t_e} \quad (6)$$

being t_R the retention time and t_e the time spent by a species molecule in the interstitial volume. k_1 is connected to the more often employed phase retention factor, k , via:

$$k_1 = \frac{(1 + k)\epsilon_{tot}}{\epsilon_e} - 1 \quad (7)$$

where ϵ_{tot} ($= V_0/V_{col}$, being V_0 the thermodynamic void volume) is the total column porosity. In place of the traditional Knox parallel zone model (also referred to as residence time weighted model) very often used in LC for the interpretation of D_{eff} [5,13,24,25], in this work we made use of the more advanced Effective Medium Theory (EMT) [26], which allows for a more physically-sound description of diffusion through complex composite porous media [10,11]. Among the many EMT models available in literature, the simplest Maxwell's expression of the effective longitudinal diffusion in fully porous ordered and random sphere packings is written as [10,11,15,27–30]:

$$D_{eff} = \frac{1}{\epsilon_e(1 + k_1)} \left[\frac{1 + 2(1 - \epsilon_e)\beta}{1 - (1 - \epsilon_e)\beta} \right] D_m \quad (8)$$

where β is the so-called polarizability constant:

$$\beta = \frac{\alpha_{part} - 1}{\alpha_{part} + 2} \quad (9)$$

and α_{part} is the relative permeability:

$$\alpha_{part} = \frac{D_{part} K_p}{D_m} \quad (10)$$

where D_{part} is the overall diffusion coefficient through the porous particles (including diffusion in the stagnant mobile phase and surface diffusion) and K_p is the whole-particle volume (V_{part})-based equilibrium constant, that is:

$$K_p = \frac{m/V_{part}}{C_m} \quad (11)$$

where m and C_m represent the mass of the adsorbed species and the equilibrium concentration in the mobile phase, respectively. Therefore, operatively, K_p can be calculated by:

$$K_p = \frac{k_1 \epsilon_e}{1 - \epsilon_e} \quad (12)$$

Other EMT models, such as for instance the Torquato's one, allows in principle for a more accurate estimation of these parameters. However, under the experimental conditions employed in this work (namely, retention factor always larger than 0.5), it has been demonstrated [12,28,29] that the difference between the simple Eq. (8) and the Torquato's model is negligible (see also later on).

The kinetic c_s term appearing in Eq. (1) describes the mass transfer across the stationary phase. Since there is absence of flow inside particles, the mass transfer coefficient across the stationary phase is velocity-independent, which makes it easier to establish theoretically-sound expression for this contribution [16]. Following Giddings [13], for fully porous spherical particles this term is commonly expressed as [15,22]:

$$c_s = \frac{1}{30} \frac{k_1}{(1 + k_1)^2} \frac{D_m}{D_{part}} \quad (13)$$

Finally, the eddy dispersion term, $a(v)$ in Eq. (1), is caused by the erratic flow profile in the through-pores of the packed bed. It includes trans-channel eddy dispersion, short-range inter-channel eddy dispersion, trans-column eddy dispersion. Despite the fundamental work of Giddings culminated in the well-known coupling theory [13], there is still considerable debate in literature regarding the values of the geometrical parameters needed to describe the complex structures of packed beds [31]. Much work in this direction has been done by Tallarek's group with a very sophisticated

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