



Transport properties and size exclusion effects in wide-pore superficially porous particles

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HIGHLIGHTS

- Size exclusion significant when molecule-sol size ratio increased from 0.025 to 0.1.
- Size exclusion effects include correlation between concentration and void fraction.
- Convection dominates near the hull for larger molecules with small diffusion rates.
- Flux well predicted by molecular diffusion rate deeper within SPP.
- Time scale for molecular first passage to given depth well predicted by diffusion.
- Intraparticle age not as well predicted by diffusion.
- Intraparticle age distribution dominated by young molecules near the hull.
- Cumulative residence time characterized by multiple short visits to first sol layer.

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ABSTRACT

The effects of hydrodynamic radius on the transport of solute molecules in packed beds of wide-pore superficially porous particles (SPP) are studied using pore-scale simulation. The free molecular diffusion rate varies with radius through the Stokes-Einstein relation. Lattice Boltzmann and Langevin methods are used to model fluid motion and the transport of an ensemble of solute molecules in the fluid, providing statistics on solute concentration, flux, molecule age and residence time, as a function of depth in the SPP. Intraparticle effective diffusion and bed dispersion coefficients are calculated and correlated with the hydrodynamic radius and accessible porosity.

The relative importance of convection and diffusion are found to depend on the molecule (tracer) size through the diffusion rate, and convection effects are more significant for larger, slower-diffusing molecules. When larger molecules are utilized, the intraparticle concentration is reduced in proportion to the local particle porosity, leading to a natural definition of the accessible porosity used in size exclusion chromatography (SEC). Although the pore shape is complex, the SEC constant K can be calculated directly from simulation. Simulation demonstrates that the effective diffusion coefficient is elevated near the particle hull, which is largely open to interstitial flow, and decreases with depth into the particle. All molecules studied here have transport access to the entire particle depth, although the accessible volume at a given depth depends on their size. The first passage time into the particle is well predicted by the diffusion rate, but residence time is influenced by convection, shortening the average visit duration. These results are of interest in “perfusion” chromatography where convection is thought to increase separation efficiency for large biomolecules.

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1. Introduction

Wide-pore superficially porous particles (SPPs) are now being utilized as a platform for separating large biomolecules and indus-

trial polymers using high performance liquid chromatography (HPLC) (Wagner et al., 2017). The morphology of SPPs includes an inert, nonporous solid core with an outer layer of porous material where chromatographic retention takes place. The performance and mechanism of smaller-pore SPPs relative to fully porous particles (FPPs) has been discussed in a number of publications of which a few are cited here (Gritti et al., 2007, 2010; Wang

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et al., 2012; Schuster et al., 2012; Hayes et al., 2014). In addition to the standard method of gradient elution chromatography, commonly used for biochemical separations, size exclusion chromatography (SEC) has recently been explored (Schure and Moran, 2017; Pirok et al., 2017; Wagner et al., 2017) using wide-pore SPPs. To improve and optimize the performance of this class of materials, the transport of solute molecules into and out of pores of these particles must be understood for both gradient elution LC and SEC.

The outermost layer of a typical wide-pore SPP is a highly porous interface between the interstitial fluid region and shell media, and constitutes a significant fraction of the shell volume (Schure et al., 2017). In SPPs, the solid core typically ranges from 60% to 80% of the particle radius. Thin shells facilitate faster mass transport between the retentive region and the interstitial region. This leads to higher chromatographic performance through less zone broadening.

A number of recent studies have examined aspects of the fundamentals of separations in porous material as a function of the solute tracer to pore size ratio, $\lambda \equiv r_{\text{mol}}/r_{\text{pore}}$. For example, Wernert et al. (2010) presented plate height data under retentionless conditions with probes of different size using silica-based columns. The data showed that zone broadening increased dramatically as λ increased. Effective diffusion was predicted using a restricted diffusion model from filtration theory (Renkin, 1954), modified with novel expressions for size-dependent porosity and tortuosity that improved the predictions for larger values of λ . The effect of molecule size in restricted diffusion is well-known from theoretical studies of pore diffusion (Brenner and Gaydos, 1977; Dechadilok and Deen, 2006; Carta and Jungbauer, 2010). In a recent study of size exclusion in silica monolithic media, Brownian Dynamics (BD) was used to evaluate effective diffusion in reconstructed media for a wide range of λ , and the results were compared with standard filtration theory (Hlushkou et al., 2017). The agreement was good for small values of λ but, like Wernert et al. (2010), they found a straightforward application of theory tended to overpredict effective diffusion for larger values of λ . Experimental and simulation results on pore diffusion were compared in Langford et al. (2006) using different media and probe sizes. BD simulations were conducted in reconstructed digital chromatographic media, and the same media were also analyzed to create network models of pore connectivity. The expected decreasing relationship between effective diffusion and probe size was observed in both simulations and experiments. Among their conclusions, the authors noted the agreement was strongest for media where structural sampling and reconstruction was most representative, e.g., where the media was more homogeneous.

A number of studies, including Koku et al. (2012) in addition to those mentioned above, have demonstrated the ability of BD to recover fundamental structural and transport properties of actual supports which have been imaged and reconstructed at the pore length scale. Similar methods are used here to quantify mass transport between SPP and the surrounding interstitial fluid in a packed bed. But in the present case, the simulated media is a random packing of model SPPs rather than reconstructed digital media. The model SPP is compared with its physical counterpart in Schure et al. (2017), along with the construction of the SPP packed media and a detailed study of fluid flow at the pore scale. The mass transport results in the present work utilize the flow fields from that study and the flow conditions are similar to those used in HPLC. The use of a well-characterized particle allows the results to be easily analyzed as a function of depth in the particles, leading to a better understanding of the size exclusion and pore diffusion mechanisms in wide-pore SPPs used in chromatography.

In the present study, identical simulations are performed using solute molecules of different radii in a single realization of a packed

bed of SPPs. The calculations are computationally intensive because two important length scales must be resolved; the sol particles (shell media) and the SPP particle itself. Hence, the computational fluid dynamics grids tend to be quite large. A related factor is that BD simulations and related methods are constrained to fairly small space and time steps, and the number of steps required to explore the pore space grows inversely with the diffusion coefficient for a given solvent flow rate.

The simulation results are organized around four topics: (1) intraparticle concentration as a function of depth in the particle and molecule radius, (2) flux within the particle as a function of depth, (3) dispersion in the packed bed and (4) solute molecule residence time in the particle. The results on concentration provide a very clear picture of the size exclusion effect and reveal a relationship between the local concentration and porosity, given explicitly as a function of shell depth. The results on flux show the role of convection near the particle hull and illustrate an approach for calculating effective diffusion from the unidirectional flux of molecules through a spherical interface. The results on dispersion in the packed bed are pre-asymptotic, but illustrate the divergence between packed beds of solid versus porous particles. The results on residence time include an analysis of mean first passage time and mean age versus depth in the particle, as well as the cumulative intraparticle residence time. The practical interpretation of these results regarding biomolecule separations is discussed in the conclusion.

2. Models and methods

2.1. SPP packed bed model

The model particle consists of a solid spherical core, $r_c = 1.650 \mu\text{m}$, surrounded by a porous shell comprising a random packing of 12,209 spherical sol particles. The sol particles have radius $r_{\text{sol}} = d_{\text{sol}}/2 = 57.5 \text{ nm}$. There are approximately four layers of sol particles in the shell. The hull is defined as a bounding sphere around the shell with radius $r_h \approx 2.15 \mu\text{m}$.

The physical particle that serves as the basis for the model SPP has a mean pore radius $r_{\text{pore}} \approx 50 \text{ nm}$, which was obtained by nitrogen adsorption techniques (Schure et al., 2017). This pore radius is on the order of the sol radius. The pore size of the model SPP varies significantly in the shell and is better represented as a range, based on the intraparticle nearest-surface distribution (NSD). The NSD is the probability density for the distance from a point in the fluid to the nearest solid surface. It has a single mode, $r \approx 0.04 d_{\text{sol}}$, and ranges up to $r \approx 0.8 d_{\text{sol}}$, which reflects the porous hull region. The NSD is shown in Fig. 4 of Schure et al. (2017). The model SPP porosity is described in Section 3.1 as a function of depth in the shell.

A random packing of SPPs was simulated by replacing the spheres in a random packing of solid spheres with SPPs of the same radius. The SPP random packing is shown in Fig. 1. The original packing of solid spheres was generated by a Monte-Carlo (MC) compression algorithm in a cubic bounding box using periodic boundary conditions (PBCs). The final configuration has a box dimension $L = 9.35 r_h$ and porosity of 36%. After replacing the solid spheres with randomly rotated SPPs, the spaces between particles were no longer closely packed because the SPP hull is a porous boundary. The bounding box was therefore compressed by further MC iterations, reducing its dimensions by 1% or approximately $3r_{\text{sol}}$. The resulting interstitial region of the SPP bed is 34% of its bounding box volume. The total packed bed porosity, ϵ_T , is the sum of two contributions: the interstitial void space ϵ and the intraparticle void space, ϵ'_p , expressed as a fraction of total bed

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