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PII: S0021-9673(18)31069-0
DOI: https://doi.org/doi:10.1016/j.chroma.2018.08.049
Reference: CHROMA 359645

To appear in: *Journal of Chromatography A*

Received date: 23-4-2018
Revised date: 10-8-2018
Accepted date: 21-8-2018

Please cite this article as: Qile P. Chen, Mark R. Schure, J. Ilja Siepmann, Using molecular simulations to probe pore structures and polymer partitioning in size exclusion chromatography, <*![CDATA[Journal of Chromatography A]]*> (2018), https://doi.org/10.1016/j.chroma.2018.08.049

# Using Molecular Simulations to Probe Pore Structures and Polymer Partitioning in Size Exclusion Chromatography

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## Abstract

Molecular simulations have been extensively utilized to understand and predict the polymer partitioning in size-exclusion chromatography (SEC). However, idealized pore models (e.g., cylindrical, spherical, and slit pores) were often used to represent the porous media in an SEC column, which leads to significant deviations in describing the geometry and the size of the pores. In this work, several complex pore models were derived from body-centered cubic, random, and gel packing of monodisperse spherical sol particles using simulation methodology. The mechanical stabilities of these structures were determined based on particle coordination numbers. Pore size distributions of these porous structures were compared to a commercially available, wide-pore superficially porous particle. Then, Gibbs ensemble Monte Carlo simulations were performed to compute the pore-to-bulk partitioning coefficient $K_{\mathrm{SEC}}$ of a polymer chain with complex pore models. The effects of particle size, packing structure, and porosity on $K_{\mathrm{SEC}}$ were explored. In addition, structural analysis provides insight into the conformation of polymers in the pores and its effect on the partitioning behavior. This study promotes the understanding of pore structures in SEC columns and enables more accurate predictions of $K_{\mathrm{SEC}}$ with less ambiguity in pore geometry.

## Highlights

- Monte Carlo simulation methods were employed to generate various pore structures.
- Compared size distribution of pore structures with that of an experimental column.
- Calculated the partition coefficient of polymers for the generated pore structures.
- Polymers with and without excluded volumes were used in the simulations.

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*Preprint submitted to Elsevier* *January 23, 2018*