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Simulating Retention in Gas-Liquid Chromatography

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Abstract

Accurate predictions of retention times, retention indices, and partition constants are a long sought-after goal for theoretical studies in chromatography. Configurational-bias Monte Carlo (CBMC) simulations in the Gibbs ensemble using the Transferable Potentials for Phase Equilibria–United Atom (TraPPE–UA) force field have been carried out to obtain a microscopic picture of the partitioning of 10 alkane isomers between a helium vapor phase and a squalane liquid phase, a prototypical gas-liquid chromatography system. The alkane solutes include some topological isomers that differ only in the arrangement of their building blocks (e.g., 2,5-dimethylhexane and 3,4-dimethylhexane), for which the prediction of the retention order is particularly difficult. The Kovats retention indices, a measure of the relative retention times, are calculated directly from the partition constants and are in good agreement with experimental values. The calculated Gibbs free energies of transfer for the normal alkanes conform to Martin's equation which is the basis of linear free energy relationships used in many process modeling packages. Analysis of radial distribution functions and the corresponding energy integrals does not yield evidence for specific retention structures and shows that the internal energy of solvation is not the main driving force for the separation of topological isomers in this system.