

# Solubility and Molecular Conformations of *n*-Alkane Chains in Water

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Numerous experimental studies have been conducted to determine the solubility of *n*-alkanes in water, but the approximately exponential decrease in solubility with carbon number renders the experimental determination of long chain solubilities exceedingly difficult [1], leading to poor agreement between different experimental data sets beyond *n*-undecane (C<sub>11</sub>) and almost no reliable data beyond *n*-hexadecane (C<sub>16</sub>). Computer simulations provide a method to determine the long chain solubilities under precisely specified conditions, but due in part to the severe sampling difficulties associated with the Widom insertion of long chains, have only been conducted for the lighter chains. We present a heteropolymer generalization of the incremental Widom insertion technique [2] combined with replica exchange molecular dynamics simulations [3] to obviate these sampling problems and provide a reliable determination of *n*-alkane solubilities up to *n*-docosane (C<sub>22</sub>). Agreement of our results with experimental data for the lighter chains is excellent and the results for the heavier chains are, to our knowledge, the first ever reported. Henry's constant exhibits a maximum as a function of chain length around *n*-octadecane (C<sub>18</sub>), corresponding to an increasing prevalence of compact chain conformations.

A free energy landscape analysis of the chain conformations reveals remarkable similarities between the ideal-gas and solvated phase landscapes, suggesting that solvated chain conformations are driven primarily by ideal-gas statistics. We find no evidence for hydrophobic collapse of *n*-alkane chains shorter than *n*-eicosane (C<sub>20</sub>). The primary effect of the solvent is the appearance of a barrier of order  $k_B T$  between the free energy basins corresponding to compact and extended chain conformations, which is associated with the onset of cavitation in the cores of compact conformations. Our findings are robust to non-trivial modification of the potential model, suggesting that the absence of strong solvent effects on the free energy landscapes is fundamental to relatively short ( $\leq 20$ mer) chains composed of small hydrophobic monomers, and does not depend on the precise nature of the chain interactions.

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