

Microscopic Structure and Solvation in Dry and Wet Octanol

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Abstract

Octanol–water partition coefficients are extraordinarily successful for correlating and predicting numerous processes of pharmacological and environmental importance. However, the structural details of the octanol phase and the reason why this phase can mimic the complexities of many different environments ranging from biomembranes to soil, are controversial. Configurational-bias Monte Carlo simulations in the Gibbs ensemble demonstrate that a diverse spectrum of hydrogen-bonded aggregates exists in neat and wet 1-octanol, and that water saturation substantially alters the 1-octanol environment. These simulation results are able to reconcile the conflicting views of the 1-octanol structure inferred from thermodynamic arguments, spectroscopic measurements, and diffraction experiments. Calculated partition constants allow us to establish the influence of water saturation on the solubility power of 1-octanol.

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