Adsorption of Benzene from a Dilute Aqueous Solution

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The adsorption of solutes from dilute solutions is a technically and scientifically important subject. The molecular simulation of density profiles of the solute at an absorbing wall in a dilute solution is difficult to achieve because potential barriers prevent the molecule from gaining its equilibrium position, orientation, or configuration. The calculation of the change in free energy via the potential of mean force (PMF) from molecular dynamics simulations (MD) offers a feasible way of performing this task.

For this method, a reference solute molecule is fixed at a certain position or configuration, a MD simulation is performed, and the mean force exerted on this molecule from the surface and the other fluid molecules can be calculated. The mean force is integrated along an appropriate path in order to yield the potential of mean force, which itself is directly related to the change in free energy. Finally, the density profile of the solute and its Henry's constant can be calculated from the change in free energy or potential of mean force.

The PMF method is applied here to the adsorption of benzene from dilute aqueous solutions at a carbon slit pore. Due to the low solubility of benzene in water, benzene is preferentially adsorbed at the carbon wall. Density profiles and the Henry's constant have been calculated at infinite dilution (one reference benzene molecule in pure water) and at preadsorption (several benzene molecules already adsorbed directly at the wall, but none at further distances). The results correspond with the typical S-shape of adsorption isotherms from dilute solutions. The calculated Henry's constant is in good agreement with experimental data.