

Hydration Properties of Low Molecular Weight Perfluorocarbons

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The purpose of this work is to elucidate the molecular mechanisms underlying the solubility of small fluorinated solutes in water, and how those differ from that of equivalent hydrogenated species. This is achieved through a study of the hydration properties of low-molecular-weight perfluorinated hydrocarbons, both experimentally and by molecular simulation.

Precise low pressure gas solubility data as a function of temperature was used to investigate the hydration properties of the fluorinated solutes between about 275 and 333 K. The solubility in water of two gaseous perfluorocarbons, perfluoroethane and perfluoropropane, was studied experimentally using different low pressure experimental techniques. For perfluoroethane, a high-precision extraction method was used, in which the degassed solvent was put in contact with the gas in a specially designed equilibration cell, kept at constant temperature. The amount of gas present in the liquid solution as well as in the vapor phase after equilibration was determined from pVT measurements. For perfluoropropane, an apparatus based on a saturation method was employed, in which the amount of gas dissolved is determined volumetrically at constant pressure and temperature.

It is observed that the solubility in water decreases with the size of the carbon chain. The analysis of the variation of the enthalpy and entropy of hydration with temperature of perfluoromethane, perfluoroethane, and perfluoropropane seems to indicate a different mechanism of solvation for the later. In order to clarify this point on the molecular scale, the hydration properties were calculated by a molecular dynamics simulation, using all-atom force fields both for the solute and the solvent, and following appropriate energy routes. After validating the force fields by confronting the results with the experimental data, the simulations were also used to assess the microscopic structure of the aqueous solutions of the fluorinated hydrocarbons.

The experimental and simulated data for the perfluorinated solvents are compared with similar data for the equivalent hydrocarbons which have a much larger solubility in water.