Structure and thermodynamics of nonaqueous solvation by integral equation theory

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Electronic structure theory under the influence of apolar solvents suffers from substantial methodical difficulties since in this case the solvent-induced solute polarization originates mainly from specific directional interactions and higher electric multipoles. Continuum solvation models based on the dielectric solvent response such as the PCM (polarizable continuum model) approach ignore such interactions and can therefore not adequately model solvation effects in nonaqueous environments. The embedded cluster reference interaction site model (EC-RISM [1]) retains the granularity of the solvent and represents a microscopically detailed and therefore improved approach towards solvation modeling. EC-RISM is based on a self-consistent solution of solvent distribution functions described by 3D-RISM integral equation theory and solute electronic structure by mapping the solvent charge distribution onto discrete, solute-embedding point charges. In aqueous solution EC-RISM theory is capable of calculating pK_a shifts[1] and tautomer ratios relatively fast and with high accuracy [2].

Here we outline the strength of the integral equation model by studying nondipolar benzene and hexafluorobenzene solutions. In particular, the thermodynamics of differential solvation is quantified for small molecules dissolved in these media. We show that EC-RISM is capable of predicting the correct tendency of transfer free energies, in contrast to PCM calculations which are not satisfactory for quadrupolar solvents. Moreover, we delineate the importance of intramolecular electronic polarization for explaining the data.
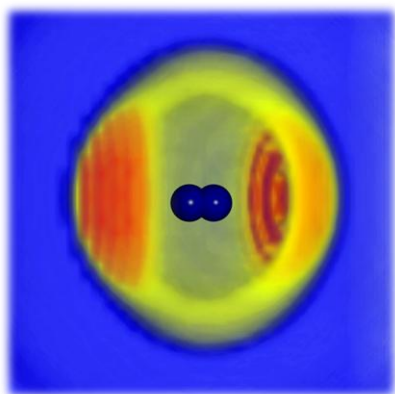

Fig. 1. Solvent distribution for benzene carbon atoms around nitrogen computed with exact electrostatic potential.
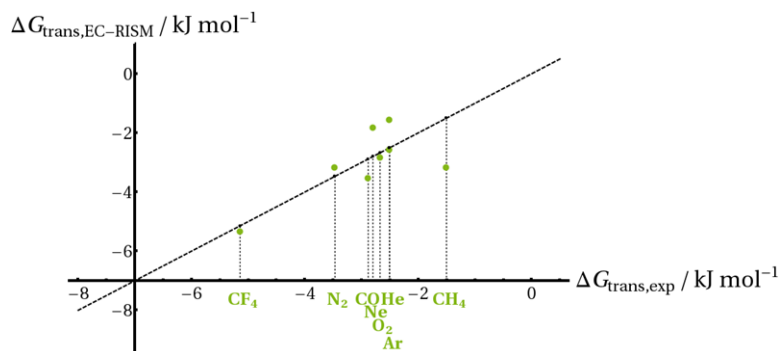

Fig. 2. Calculated vs. experimental transfer Gibbs free energies for several simple gases from B3LYP/6-311G(d,p)/PCM// B3LYP/6-311G(d,p)/EC-RISM/PSE-1 calculations.

[1]   T. Kloss, J. Heil, S. M. Kast , *J. Chem. Phys. B* **2008**, *112*, 4337.
[2]   S. M. Kast, J. Heil, S. Güssregen, K. F. Schmidt, *J. Comput.-Aided Mol. Des.* **2010**, *24*, 343.