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Using a COSMO-based cubic equation of state to predict solvation quantities of molecules and free radicals in liquid and supercritical solvents

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Kinetic generators like EXGAS RMG, MAMOX, NetGen, REACTION, and GENESYS provide a detailed and reliable representation of the complex free radical chain mechanism associated with gas phase combustion. Following the work of Jalan and co-authors [1], our group recently proposed an accurate method that uses a cubic equation-of-state (EoS) for estimating solvation free energies that are used to adapt the gas phase kinetic model to liquid or supercritical media [2,3]. As a result, the gas phase detailed kinetic model can be used in a new range of applications, such as prediction of biofuels aging, simulation of liquid phase chemical reactor, design of supercritical power-cycle systems, simulation of wastewater and sludge treatment in supercritical media, etc. A major drawback of this approach is that the thermodynamic correction of the free radicals is approximated. In the EoS approach, it is assumed that radicals have the same solvation energy as their corresponding parent molecules (H-atom added on the radical site), which can be a source of error, especially in polar media.

With this in mind, we extended the EoS approach to deal with the solvation of free radicals. For this purpose, the cubic EoS was adapted in two ways, one to estimate the pure compound parameters of free-radicals by a new group contribution approach and another to estimate the mixture parameters based on an advanced mixing rules relying on a quantum-based continuum solvation model (COSMO-RS). Although no experimental data is needed to parameterize the proposed EoS (only predictive quantum-based calculations are used instead), it provides reliable predictions of solvation free energies, with average errors below 0.5 kcal/mol. Being an equation of state, the proposed model can also perform pure predictions of solubilities, phase equilibria, heat capacities and enthalpies for energy balances, etc [4]. The adaptation of the cubic EoS applied to free radicals appears to be extendable to any type of molecule, which can be very useful in the treatment of species for which experimental data is inexistent or extremely scarce.

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