

A new family of equations of state: COSMO-SAC-Phi

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Although very successful, activity coefficient models based on the COSMO-RS theory (1), like COSMO-SAC (2) and F-SAC (3, 4), can represent incompressible liquids only. In this lecture the COSMO-SAC-Phi method (5) will be addressed, showing how pressure effects can be included in any of these models by the addition of *free volume* or *holes*.

The COSMO-SAC-Phi method (5), inspired by *lattice fluid* ideas, consists in the inclusion of *holes* and *free volume* in COSMO-SAC, as schematically shown in Fig. 1. However, there is no need to actually define a lattice and there is no explicit coordination number (*i.e.*, a number of nearest neighbors interacting with a given molecule). For given temperature, volume, and mole numbers, the computational cost is the same required by any COSMO-based model. In principle, the method can be combined with any COSMO-RS, COSMO-SAC, or F-SAC variant.

By adding free volume, compressible fluids can be modeled allowing to represent pressure-volume relations from liquid to gas. Dispersion and free-volume parameters are currently estimated from pure compound data, attempts to predict these parameters should be pursued in the future. Results for the correlation of pure compound saturation pressure and liquid volume are shown in Fig. 2. Typical predictions for vapor-liquid equilibrium (VLE) data are shown in Fig. 3. For liquid-liquid equilibrium (LLE) predictions, some results can be seen in Fig. 4. In these figures COSMO-SAC-Phi is compared to Soave-Redlich-Kwong with Mathias-Copeman α -function (6) - SRK-MC. For mixture VLEs, the classical van der Waals mixing rules were considered - SRK-MC+vdW. For LLE cases, the benchmark was UNIFAC-LLE (7). All COSMO-SAC results shown here use the open-source LVPP sigma-profile database (8) with the GMHB1808 parametrization, both freely available at github.com/lvpp/sigma.

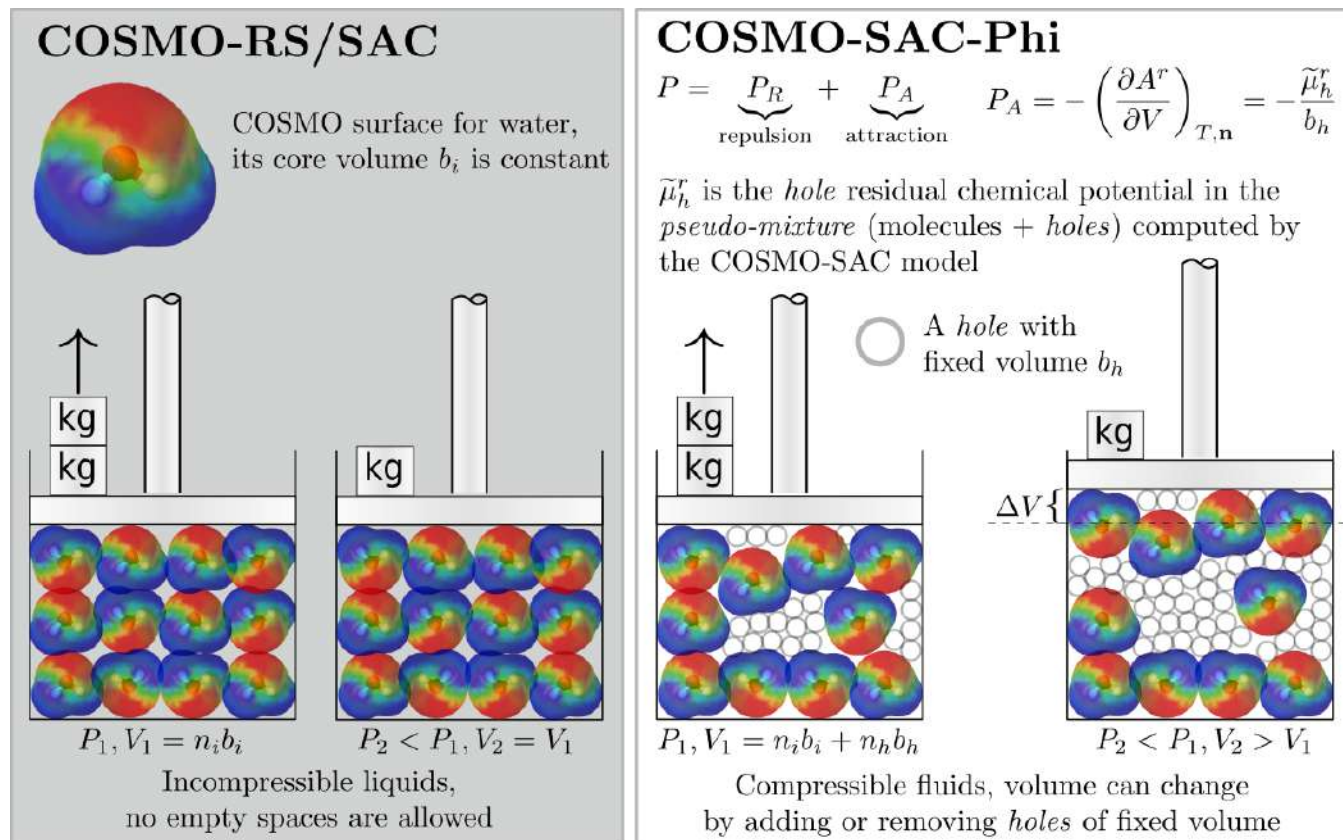


Fig. 1. COSMO-RS/SAC and COSMO-SAC-Phi schematic representations, empty spaces are allowed in the later model by the addition of holes and free volume.

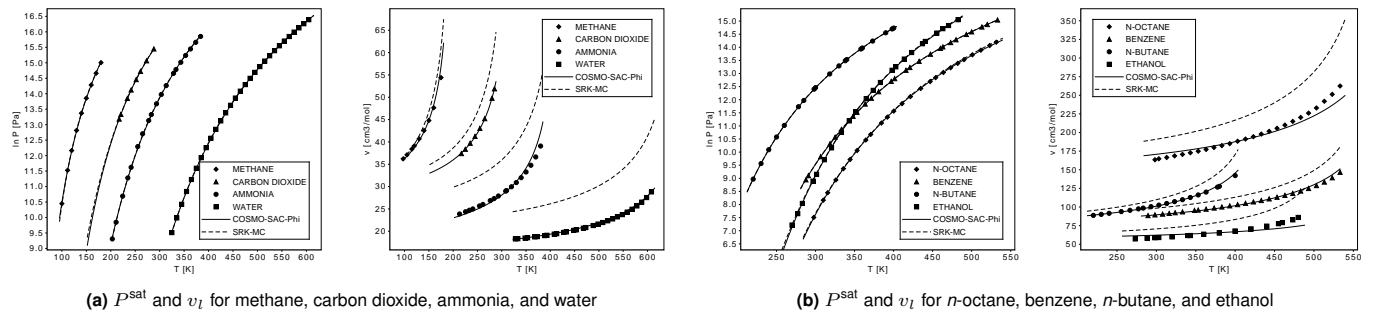


Fig. 2. Pure compound data correlation for various substances, ranging from water, ammonia, etc., up to *n*-octane.

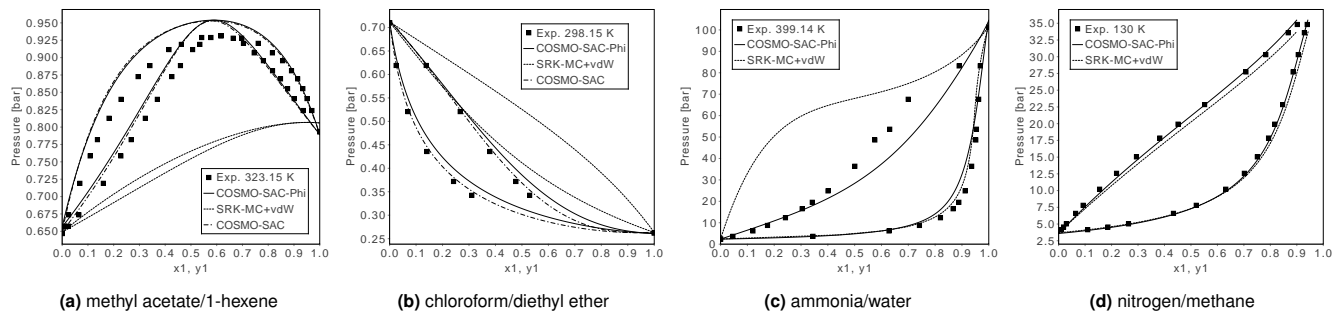


Fig. 3. Vapor-liquid equilibrium predictions from low pressures up to 100 bar with both negative and positive deviations from Raoult's law.

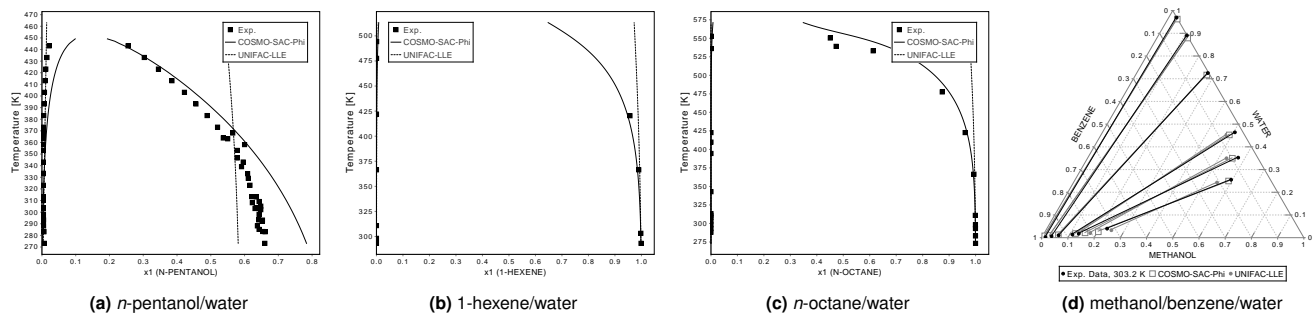


Fig. 4. Predicted liquid-liquid equilibrium data for binary and ternary mixtures.

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