

## **Modeling the phase equilibria of refrigerant fluids with the COSMO-SAC and COSMO-RS approaches. Application to process simulation.**

Patrice Paricaud<sup>1</sup>, Olivier Baudouin<sup>2</sup>, Abdelatif Baba-Ahmed<sup>3</sup>, Jiri Janecek<sup>1</sup>, Celine Houriez<sup>4</sup>, Christophe Coquelet<sup>4</sup>, Johnny Deschamps<sup>1</sup>, Laurent Catoire<sup>1</sup>, Didier Dalmazzone<sup>1</sup>.

<sup>1</sup>ENSTA ParisTech, Unité Chimie et Procédés, 828 Boulevard des Maréchaux, 91762 Palaiseau Cedex, France.

<sup>2</sup>ProSim, Stratège Bâtiment A, 51 Rue Ampère, F-31670 Labège, France.

<sup>3</sup>Arkema, CETIA Chemin de la Lône - BP 32, 69492 Pierre-Bénite Cedex, France .

<sup>4</sup>Mines ParisTech, CTP – Centre Thermodynamique des Procédés, 35 Rue Saint Honoré, 77305 Fontainebleau Cedex, France.

On account of the constraints imposed by the European and International legislations, the refrigerant industry must constantly find alternative refrigerant fluids that have lower impacts on the global warming of Earth and Ozone layer. Working with refrigerant blends is often preferable to pure component fluids for energy saving and flexibility of operation. In order to select the optimal mixture composition for the design and operation of a refrigeration process, it is necessary to know the phase diagram and thermodynamic properties of mixtures. Vapor-liquid equilibria (VLE) and the location of azeotropes must be accurately known.

In this work three different thermodynamic models based on the COSMO approach have been used to predict the phase equilibria of mixtures of refrigerant molecules: the COSMO-RS model developed by Klamt and co workers [1, 2], the 2002 version of COSMO-SAC model [3], and the COSMO-SAC-dsp model [4] that includes a dispersion term. The vapor-liquid equilibria can be reasonably well predicted by the COSMO-RS model, however bad predictions are obtained with COSMO-SAC 2002. In particular, the COSMO-SAC model is unable to predict the azeotropic behavior observed in mixtures of alkanes and fluorinated molecules. By adjusting some universal parameters, it is possible to obtain reasonable predictions with the COSMO-SAC dsp model.

We have developed a dynamic link library (dll) containing the COSMO models and that can be used within the expert modes of the Simulis<sup>®</sup> thermodynamic server. This server is embedded in all ProSim simulation software and then these models can be used in all of them, e.g. Prosim plus<sup>®</sup> steady state process simulation software. The standard version of Simulis<sup>®</sup> Thermodynamics is provided as an add-in in Microsoft<sup>®</sup> Excel or as a toolbox in MATLAB<sup>®</sup> and enables the user to run complete thermodynamic calculations in these applications. Another main benefit of Simulis<sup>®</sup> Thermodynamics is its CAPE-OPEN compliance through its implementation of the CAPE-OPEN standardized interfaces. CAPE-OPEN packages that use our own codes of COSMO-SAC have been generated with Simulis<sup>®</sup> Thermodynamics, and used into other process simulation software such as Aspen<sup>™</sup> plus and COFE, to perform simulation of separation units.

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[3] S.T. Lin, S.I. Sandler, A priori phase equilibrium prediction from a segment contribution solvation model, Ind. Eng. Chem. Res., 41 (2002) 899-913.

[4] C.-H. Hsieh, S.-T. Lin, J. Vrabec, Considering the dispersive interactions in the COSMO-SAC model for more accurate predictions of fluid phase behavior, Fluid Phase Equilib., 367 (2014) 109-116.