



# **COSMO-RS Manual**

*ADF Modeling Suite 2016*

**[www.scm.com](http://www.scm.com)**

November 18, 2016



<b>1</b>	<b>General</b>	<b>1</b>
1.1	Introduction . . . . .	1
1.2	Release 2016 . . . . .	2
<b>2</b>	<b>COSMO-RS and COSMO-SAC</b>	<b>3</b>
2.1	COSMO-RS theory . . . . .	3
2.2	COSMO-SAC 2013-ADF . . . . .	6
2.3	Calculation of properties . . . . .	6
<b>3</b>	<b>COSMO result files</b>	<b>11</b>
3.1	ADF COSMO calculation . . . . .	11
3.2	COSMO-RS Database ADFCRS-2010 . . . . .	15
3.3	COSMO-RS Ionic Liquid Database ADFCRS-IL-2014 . . . . .	16
3.4	MOPAC COSMO calculation . . . . .	17
<b>4</b>	<b>The COSMO-RS program</b>	<b>19</b>
4.1	Running the COSMO-RS program . . . . .	19
4.2	COSMO-RS and COSMO-SAC parameters . . . . .	19
4.3	Compounds . . . . .	24
4.4	Temperature . . . . .	25
4.5	Pressure . . . . .	25
4.6	Molar fractions and mass fraction . . . . .	26
4.7	Properties . . . . .	26
4.8	Analysis . . . . .	30
<b>5</b>	<b>Scripting with COSMO-RS</b>	<b>33</b>
5.1	ADFprep: construct an ADF COSMO results file . . . . .	33
5.2	CRSprep: generate (multiple) COSMO-RS jobs . . . . .	33
5.3	ADFreport: generate report . . . . .	35
5.4	KF utilities for COSMO-RS . . . . .	36
5.5	Scripting Examples . . . . .	37
<b>6</b>	<b>Required Citations</b>	<b>49</b>
6.1	General References . . . . .	49
6.2	External programs and Libraries . . . . .	49
<b>7</b>	<b>References</b>	<b>51</b>
<b>8</b>	<b>Keywords</b>	<b>53</b>
	<b>Index</b>	<b>55</b>



## 1.1 Introduction

The ADF COSMO-RS (COnductor like Screening MOdel for Realistic Solvents) program is a program that can be used for calculating thermodynamic properties of (mixed) fluids. The COSMO-RS method was developed by Klamt and coworkers [1-3 (page 51)]. On the basis of the framework of COSMO-RS, Lin and Sandler [8 (page 51)] suggested a variation, the COSMO-SAC (where SAC denotes segment activity coefficient) model. There are different implementations of COSMO-RS and COSMO-SAC or derivatives, and different parametrizations. The implementation of COSMO-RS in ADF is described in Ref. [4 (page 51)], which is based on the COSMO-RS method developed by Klamt et al. [2 (page 51)]. The implementation of COSMO-SAC 2013-ADF in ADF is based on the COSMO-SAC model developed by Xiong et al. [9 (page 51)].

Our COSMO-RS capabilities are summarized on the product page (<https://www.scm.com/product/cosmo-rs>).

With COSMO-RS it is possible to use a thermodynamically consistent combinatorial contribution to the chemical potential as is used in Ref. [3 (page 51)], and a temperature dependent hydrogen bond interaction, also described in Ref. [3 (page 51)]. The parameters in the paper [2 (page 51)] were reparametrized for ADF, see Ref. [4 (page 51)] for details.

The COSMO-SAC 2013-ADF parameters in Ref. [9 (page 51)] were optimized for use with ADF COSMO result files. COSMO-SAC 2013-ADF is an improved COSMO-SAC method compatible to ADF and different than previous COSMO-SAC methods. The main difference that the COSMO-SAC 2013 model includes a dispersion contribution in the mixture interaction. Previous COSMO-SAC methods are described in Refs. [6,7 (page 51)].

The ADF COSMO-RS (and COSMO-SAC) command line program is called *crs*. The main authors of this program are Cory Pye (Saint Mary's University, Halifax NS Canada) and Jaap Louwen (Albemarle Corporation). COSMO-SAC 2013-ADF was implemented in collaboration with R. Xiong and R.I. Burnett (Sandler group, University of Delaware, Newark, USA). Previous COSMO-SAC methods were implemented by Erin McGarrity (TU Delft, the Netherlands). The COSMO-RS GUI *ADFcrs* contains an input builder for COSMO-RS and can visualize results, see the COSMO-RS GUI tutorials and the COSMO-RS GUI reference manual.

COSMO-RS (and COSMO-SAC) use the intermediate results from quantum mechanical (QM) calculations on individual molecules to predict thermodynamic properties of mixtures of these molecules, for example, solubility. There are a fair number of reports of accurate prediction by COSMO-RS of thermodynamic properties in general in the literature. Many of these have been written by Klamt and co-workers, see Ref. [3 (page 51)] and references therein.

There are also empirical methods like UNIFAC that can predict thermodynamic properties (including the activity coefficients). These methods contain group specific parameters and are parametrized against a large data base. They will often do better than COSMO-RS or COSMO-SAC methods (especially, of course, if the system of interest was part of the data base used for parameter estimation). However, these methods cannot handle every type of molecule. In particular when unusual combinations of functional groups occur (such as in drug molecules), no parametrization is available. COSMO-RS and COSMO-SAC methods, on the other hand, only feature general parameters not specific to chemical groups or functionalities. All that is required is that a quantum mechanical calculation can be done on the molecule. Therefore, COSMO-RS or COSMO-SAC can be a valuable tool for the prediction of chemical engineering

thermodynamical properties, like, for example, partial vapor pressures, solubilities, and partition coefficients. An additional advantage of COSMO-RS and COSMO-SAC over empirical methods is that the molecules dissolved may in fact be transition states of a chemical reaction. This follows from the fact that all that is required is that one can do a QM calculation on the solute and QM on a transition state has become standard in the last two decades. This affords a unique opportunity to predict the thermodynamics of a reaction including, for instance, the balance between kinetically and thermodynamically favored reaction pathways as a function of the solvent used.

## 1.2 Release 2016

The major changes of COSMO-RS 2016 in comparison to COSMO-RS 2014 are described here.

- *vapor pressures calculation consistent with the COSMO-SAC 2013-ADF method* (page 21)
- *Scripting with COSMO-RS* (page 33)
  - *ADFPrep: construct an ADF COSMO results file* (page 33)
  - *CRSprep: generate (multiple) COSMO-RS jobs* (page 33)
  - *ADFPreport: generate report* (page 35)
  - *KF utilities for COSMO-RS* (page 36)
  - *Scripting Examples* (page 37)
- *The COSMO-RS Ionic Liquid Database ADFCRS-IL-2014* (page 16)
  - See also the COSMO-RS GUI Tutorial: The COSMO-RS model for Ionic Liquids

## COSMO-RS AND COSMO-SAC

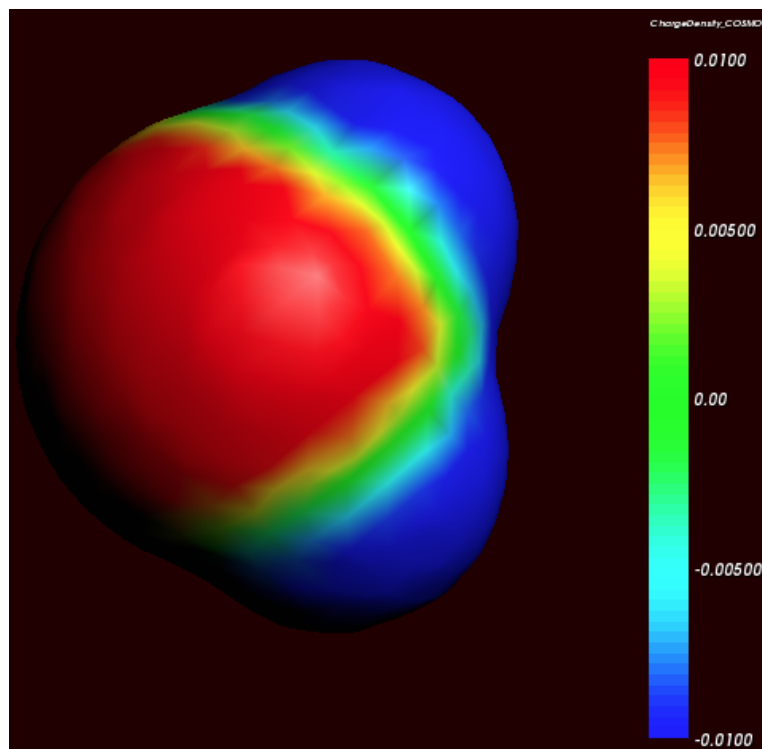
### 2.1 COSMO-RS theory

Below some of the COSMO-RS theory is explained, but a more complete description can be found in Refs.[2 (page 51)] and [3 (page 51)].

Although in principle all of chemistry can be predicted by appropriate solutions of the Schrödinger Equation, in practice due to the extreme mathematical complexity of doing so only the smallest systems can be computed at an accuracy rivaling that of the most accurate experiments. However, with suitable approximations, for isolated molecules of up to a few hundred atoms these days quite reasonable results can be obtained. Of course, this means that direct computation of thermodynamic properties is out of reach. Thermodynamic properties can only be computed as an average over a large number of configurations of a large number of molecules. To address this, people have typically resorted to so-called Molecular Dynamics (MD) or Monte Carlo (MC) methods where configurations are generated either by numerically simulating the atomic motions over discrete time steps or by random generation, in either case using empirical molecular models parametrized against quantum mechanical calculations and experimental data to compute energies. However, even these approaches often fall short in generating sufficiently large ensembles, and there is little chance of that situation improving dramatically in the near future.

Around 1995, Andreas Klamt, then working for Bayer, hit upon an approach that made it possible to compute the details of molecules quantum mechanically and subsequently use these details in an approximate statistical mechanics procedure [1 (page 51)]. This approach is called COSMO-RS (COnductor like Screening MOdel for Realistic Solvents) and has proven to be quite powerful. It may currently be the best link between the world of chemical quantum mechanics and engineering thermodynamics.

Thermodynamic reference states can be chosen arbitrarily. They do not even have to be physically realizable, as long as it is consistently used. We are at liberty to choose as reference state a molecule embedded in a perfect conductor, that is a material with an infinitely large dielectric constant ('the perfectly screened state'). Suppose a molecule A resides in a molecule shaped cavity. Everywhere outside of this cavity is conductor material. Although it would be hard to realize this in practice, it is relatively easy to do quantum mechanical calculations on this hypothetical state. Since the molecule will in general have a charge distribution and therefore possess an electric field, it will polarize the embedding medium. That will result in another electric field, given by a charge distribution on the surface of the molecule shaped cavity. This charge distribution is generated by the quantum mechanical calculations, for example with ADF if one uses COSMO. From now on the surface of the molecule shaped cavity will be called molecular surface, and the volume of the molecule shaped cavity will be called molecular volume.



Cosmo charge density on the COSMO surface of water (picture made with ADFview).

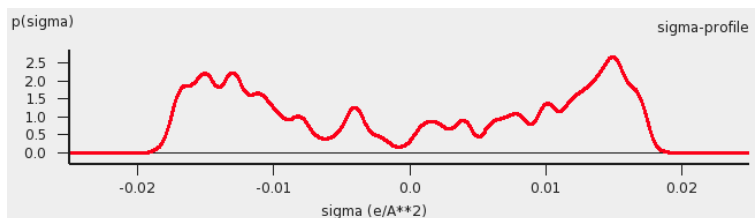
Although the actual charge distribution on the molecular surface will be highly detailed, let us for the moment consider the molecular surface as consisting of segments with a constant charge density (i.e. the detailed charge distribution averaged over segments). Now instead of the single molecule A consider, as an arbitrary example, a fluid consisting of three types of molecules: A, B and C. In a fluid not too close to the critical temperature, the molecular surfaces present in the fluid will all be in close contact. That means that the segments of constant density introduced above are in close contact.

We now compare our molecule A in the fluid with our chosen reference state. Any segment of the molecular surface with a charge density of  $\sigma_i$  will be aligned with a segment with charge density  $\sigma_j$  of another molecule. If the two charge densities happen to be opposite (i.e.  $\sigma_i + \sigma_j = 0$ ) the charges required for achieving the perfectly screened state will vanish. However, this will not happen too often and in general an excess charge density is left of  $\sigma_i + \sigma_j$  between the two segments. From electrostatic theory it follows that this introduces an energy penalty proportional to the segment size and  $(\sigma_i + \sigma_j)^2$ . In principle this gives a way to compute the chemical potential of component A, by going over all possible conformations of a large number of molecules A, B and C (in their proper molar fractions) and do computations on the statistical ensemble. However, in practice that would be similar to doing Molecular Dynamics calculations using empirical structure models and about as computationally prohibitive. Instead, an approximation can be made that is not easily justified a priori and must be judged by the results of subsequent simulations. This assumption is that all segments in the fluid are able to make contact independent of one another. In a way it can be said, that the segments are cut loose from the original (rigid) molecular surfaces.

As one would guess, the approximation of independent segments makes the mathematics of computing ensemble properties quite tractable. In fact, computing the chemical potential of component A (or B or C) in the mixture by means of the COSMO-RS and related methods takes in the order of seconds on a normal PC (given the results of quantum mechanical calculations that may have taken days, of course). Note that the molecular surface around the molecule is divided rather arbitrarily in segments and that the assumption was that the segment of one molecule will overlap perfectly with that of another. How can this be true? The answer is that one can split up the molecular surface into segments in an infinite number of ways. However, the molecules in a fluid are always in contact with another. At any given time, molecule A will be in contact with a number of other molecules and share patches of, for example, 7 square Angstroms of its surface with each of the surrounding molecules. At that particular time, the segments will be



those patches. A split second later, of course, there will be a different set of segments. That is not a problem. One needs to do statistical mechanics with charged segments for which one needs to know how many 7 square Angstrom segments a particular molecule brings into the fluid and the probability of any segment having an average charge density  $\sigma$  (for all values of  $\sigma$ ). Both can be computed from the results of the quantum mechanical calculation on the molecule in the perfect conductor. Just to get a flavor, in the figure below the so-called  $\sigma$ -profile of water is given. These are the statistical distributions of possible segments over charge densities multiplied by the surface area of the molecular volume. The  $\sigma$ -profile relates to the detailed charge distribution on the molecular surface.



$\sigma$ -profile of water (picture made with the CRS-GUI), smoothed curve, Delley COSMO surface construction

In principle vapor pressures of pure liquids can be computed directly with COSMO-RS. COSMO-RS calculations yield the chemical potential of a component in a liquid with respect to the perfectly screened reference state. It is easy to compute the energy difference between the reference state and the gas phase by doing an additional quantum mechanical calculation (of the isolated molecule). However, often experimental vapor pressures for the pure liquid are known. Using such experimental data for pure liquids can help in predicting the correct partial vapor pressures in a mixture.

## 2.1.1 COSMO-RS combinatorial term

In Ref.[2 (page 51)] a thermodynamically inconsistent combinatorial contribution  $\mu_i^{comb}$  to the chemical potential was used:

$$\mu_i^{comb} = -\lambda RT \ln(q_{av}/\text{\AA}^2)$$

$$q_{av} = \sum_i x_i q_i$$

In this equation  $q_i$  is the surface area of the molecular volume of compound  $i$ ,  $x_i$  is the molar fraction of compound  $i$  in the solution, and  $\lambda$  is a COSMO-RS parameter.

The importance of using a thermodynamically consistent combinatorial contribution is discussed in Ref. [3 (page 51)]. In the ADF COSMO-RS program it is possible to use a thermodynamically consistent combinatorial contribution of the form (Equation C.4 of Ref.[3 (page 51)], with  $\lambda_0 = \lambda_1 = \lambda_2 = \lambda$ ):

$$\mu_i^{comb} = \lambda RT (1 - r_i/r_{av} + \ln(r_i/r_{av}) + 1 - q_i/q_{av} - \ln(q_{av}/\text{\AA}^2))$$

$$r_{av} = \sum_i x_i r_i$$

In this equation  $r_i$  is the molecular volume of compound  $i$ . In the ADF COSMO-RS program this combinatorial term is used by default, see also Ref. [4 (page 51)].

## 2.1.2 Fast approximation for COSMO-RS calculations

In the 1998 COSMO-RS model each segment of the molecular surface has a charge density of  $\sigma_v$ , but also a second charge density  $\sigma_v^\perp$ , which is a descriptor for the correlation between the charge density on the segment with its surrounding. In the original ADF COSMO-RS implementation this was treated as a 2-dimensional problem, in the fast approximation this is effectively reduced to 1-dimension. Starting from COSMO-RS 2010 this fast approximation is now the default. This approximation reduces the computation time, especially in cases of more than 1 compound.

### 2.1.3 Temperature dependent hydrogen bond interaction

In Ref.[3 (page 51)] a temperature dependent hydrogen bond interaction is suggested, which is used by default in the ADF COSMO-RS program. The temperature dependence (Equation 6.2 of Ref.[3 (page 51)]) is of the form:

$$\begin{aligned} term(T) &= T \ln[1 + \exp(20kJ/mol/RT)/200] \\ f_{hb}(T) &= term(T)/term(298.15K) \end{aligned}$$

Note that here the correct formula is used with a plus sign before 20 kJ/mol (there is a sign error in Equation 6.2 of Ref.[3 (page 51)], see online ‘List of Errata in the COSMO-RS book’ by Andreas Klamt), such that this factor goes to zero for large T. In this equation R is the gas constant and T the temperature (in Kelvin). In the ADF COSMO-RS program the hydrogen bond interaction of Ref.[2 (page 51)] is multiplied by this factor  $f_{hb}(T)$  to make the hydrogen bond interaction temperature dependent.

## 2.2 COSMO-SAC 2013-ADF

On the basis of the framework of COSMO-RS, Lin and Sandler [8 (page 51)] suggested a variation, the COSMO-SAC (where SAC denotes segment activity coefficient) model by invoking a necessary thermodynamic consistency criterion. Although there are differences, COSMO-RS and COSMO-SAC share some similarities. Later improvements of COSMO-SAC appeared, like in Refs. [6,7,9 (page 51)]. The COSMO-SAC 2013-ADF method used in ADF is the one developed by Xiong et al., which is described in detail in Ref. [9 (page 51)]. The COSMO-SAC 2013-ADF parameters in Ref. [9 (page 51)] were optimized for use with ADF COSMO result files. COSMO-SAC 2013-ADF is an improved COSMO-SAC method compatible to ADF and different than previous COSMO-SAC methods. The main difference compared to previous COSMO-SAC methods is that the COSMO-SAC 2013 model includes a dispersion contribution in the mixture interaction.

The ADF COSMO-RS program can calculate activity coefficients using the COSMO-SAC 2013-ADF model, based on Ref. [9 (page 51)]. Like in the COSMO-RS method, pure compound vapor pressures can be given as input, for example, if experimental values are available. If these values are not specified then the pure compound vapor pressure will be calculated according to the COSMO-SAC 2013-ADF model. This part of the COSMO-SAC 2013-ADF has been implemented in ADF2016. It is also possible to use some earlier COSMO-SAC methods [6,7 (page 51)], but note that the parameters in those methods were not optimized for use with ADF COSMO result files.

The COSMO-SAC 2013 model includes a dispersion contribution in the mixture interaction. This dispersion contribution is a complicated expression which also depends on the liquid molar volume of the pure compounds and on the molar volume of the mixture. The molar volume of the mixture is calculated from the pure compound liquid molar volumes assuming ideal mixing. In the input for the ADF COSMO-RS program one include for each compound the experimental pure compound liquid density (kg/L), from which the program can calculate the pure compound liquid molar volumes. If this density is not given the pure compound liquid molar volume will be calculated from its COSMO volume. Note that in the calculations with the COSMO-SAC 2013-ADF model in Ref. [9 (page 51)] often experimental pure compound liquid molar volumes were used.

## 2.3 Calculation of properties

The COSMO-RS method allows to calculate the (pseudo-)chemical potential of a compound in the liquid phase, as well as in the gas phase, see the the COSMO-RS theory that was discussed before and Ref.[2 (page 51)]. In the ADF

COSMO-RS implementation the following equations were used to calculate properties using these chemical potentials.

$$\begin{aligned}
 \sum_i x_i &= \sum_i y_i^{vapor} = \sum_i w_i = 1 \\
 w_i &= x_i M_i^{pure} / M^{ave} \\
 M^{ave} &= \sum_i x_i M_i^{pure} \\
 p_i^{pure} &= \exp\{(\mu_i^{pure} - \mu_i^{gas})/RT\} \\
 p_i^{vapor} &= x_i \exp\{(\mu_i^{solv} - \mu_i^{gas})/RT\} \\
 p^{vapor} &= \sum_i p_i^{vapor} \\
 y_i^{vapor} &= p_i^{vapor} / p^{vapor} \\
 \gamma_i &= \exp\{(\mu_i^{solv} - \mu_i^{pure})/RT\} \\
 a_i &= \gamma_i x_i \\
 G^E &= \sum_i (\mu_i^{solv} - \mu_i^{pure}) \\
 H^E &= -RT^2 \partial\{G^E/RT\}/\partial T \\
 G^E &= H^E - TS^E \\
 \Delta_{vap}H &= RT^2 / p^{vapor} \partial\{p^{vapor}\}/\partial T \\
 k_H &= 1/V_{solvent} \exp\{(\mu_i^{gas} - \mu_i^{solv})/RT\} \\
 k_H^{cc} &= 1/(k_H V_{solvent}) = \gamma_i p_i^{pure} \\
 x_i^{SOL} &= 1/\gamma_i (T > T_m) \\
 x_i^{SOL} &= 1/\gamma_i \exp\{\Delta H_{fus}(1/T_m - 1/T)/R - \Delta C_p(\ln(T_m/T) - T_m/T + 1)/R\} (T < T_m) \\
 \Delta G_{solv}^{liq-solv} &= \mu_i^{solv} - \mu_i^{pure} \\
 \Delta G_{solv}^{gas-solv} &= \mu_i^{solv} - \mu_i^{gas} + RT \ln(V_{solvent}/V_{gas}) \\
 \log_{10} P_{solv1/solv2} &= 1/\ln(10) (\mu_i^{solv2} - \mu_i^{solv1})/RT + \log_{10}(V_{solv1}/V_{solv2}) \\
 1/LFL_{mix} &= \sum_i (y_i^{vapor}/LFL_i)
 \end{aligned}$$

The above equations are not always exact, some assume perfect gas behavior, for example.

The molar fraction  $x_i$  of each compound  $i$  of the solvent should add up to 1.

With the COSMO-RS method it is possible to predict vapor pressures. In the COSMO-RS model the free energy difference between the chemical potential in the gas phase (perfect gas with a reference state of 1 bar) and the chemical potential of the liquid phase has been defined in such a way that the equation:  $p_i = \exp(\mu_i^{pure} - \mu_i^{gas})/RT$ , will give the pressure in units of bar. It is also possible to use experimental vapor pressures of pure compounds as input data for the calculation. This may increase the accuracy of the calculated vapor pressures in a mixture, for example.

In the COSMO-RS method the volume of 1 molecule in the liquid phase is approximated with the volume of the molecule shaped cavity, that is used in the COSMO calculations. In this way it is possible to calculate the volume of 1 mole of solvent molecules in the liquid phase. However, for properties that depend on such volumes, one can also use (related) experimental data as input data for the calculation.

The calculation of the boiling temperature of a solvent is performed with an iterative method. The temperature is varied until the calculated vapor pressure is within a certain threshold of the desired pressure.

Also the calculation of solubility of compound  $i$  is performed with an iterative method, since the activity coefficient  $\gamma_i$  depends on the molar fraction of this compound. The COSMO-RS method does not predict  $\Delta H_{fus}$ ,  $\Delta C_p$ , or  $T_m$ . These can be given as input data for the calculation of solubility calculations of solid compounds.

Starting from ADF2012 the Gibbs-Helmholtz equation is used to calculate the excess enthalpy of a mixture. Previously it was estimated using the misfit and hydrogen bonding energy of the mixture and its pure compounds.

Quantity	Meaning
$R$	Gas constant
$T$	Temperature
$x_i$	The molar fraction of compound i in a liquid solution
$y_i^{\text{vapor}}$	The molar fraction of compound i in the gas phase
$w_i$	The mass fraction of compound i in a liquid solution
$M_i^{\text{pure}}$	The molar mass of the pure compound i
$M^{\text{ave}}$	The average molar mass of the mixture
$\gamma_i$	Activity coefficient of compound i in a liquid solution
$a_i$	Activity of compound i in a liquid solution
$p_i^{\text{pure}}$	The vapor pressure of the pure compound i
$p_i^{\text{vapor}}$	The partial vapor pressure of compound i
$p^{\text{vapor}}$	The total vapor pressure
$\mu_i^{\text{gas}}$	The pseudochemical potential of the pure compound i in the gas phase
$\mu_i^{\text{pure}}$	The pseudochemical potential of the pure compound i in the liquid phase
$\mu_i^{\text{solv}}$	The pseudochemical potential of compound i in a liquid solution
$G^E$	The excess Gibbs free energy
$H^E$	The excess enthalpy, Gibbs-Helmholtz equation
$\Delta_{\text{vap}}H$	The enthalpy of vaporization, Clausius-Clapeyron equation
$E_i^{\text{HB pure}}$	The hydrogen bond energy of the pure compound i in the liquid phase, see Ref.[2 (page 51)]
$E_i^{\text{HB}}$	The partial hydrogen bond energy of compound i in a liquid solution
$E_i^{\text{misfit pure}}$	The misfit energy of the pure compound i in the liquid phase, see Ref.[2 (page 51)]
$E_i^{\text{misfit}}$	The partial misfit energy of compound i in a liquid solution
$\Delta G_{\text{solv}}^{\text{liq-solv}}$	The solvation Gibbs free energy from the pure compound liquid phase to the solvated phase
$\Delta G_{\text{solv}}^{\text{gas-solv}}$	The solvation Gibbs free energy from the pure compound gas phase to the solvated phase, with a reference state of 1 mol/L in both phases
$k_H$	Henry's law constant: ratio between the liquid phase concentration of a compound and its partial vapor pressure in the gas phase
$k_H^{\text{cc}}$	dimensionless Henry's law constant: ratio between the liquid phase concentration of a compound and its gas phase concentration
$k_H^{\text{px inv}}$	Henry's law constant, representing the volatility instead of the solubility, ratio between the partial vapor pressure of a compound in the gas phase and the molar fraction in the liquid phase"
$V_{\text{solvent}}$	Volume of 1 mole of solvent molecules in the liquid phase
$V_{\text{gas}}$	Volume of 1 mole of molecules in the gas phase (at 1 atm, perfect gas)
$x_i^{\text{SOL}}$	Solubility of compound i in a solvent (molar fraction)
$\Delta H_{\text{fus}}$	The enthalpy of fusion of compound i
$\Delta C_p$	The $\Delta$ heat capacity of fusion of compound i
$T_m$	The melting temperature of compound i
$\log_{10} P_{\text{solvl}/\text{solv2}}$	The logarithm of the partition coefficient P, which is the ratio of the concentrations of a compound in two immiscible solvents, solvent 1 and solvent 2
$LFL_i$	The flash point (lower flammable limit, LFL) of compound i
$LFL_{\text{mix}}$	The flash point (lower flammable limit, LFL) of a mixture, Le Chatelier's mixing rule

See also the COSMO-RS GUI tutorial for the calculation of the following properties:

- solvent vapor pressure [1, 2]

- boiling point of a solvent [1]
- partition coefficients (log P) [1, 2], Octanol-Water partition coefficients (log P<sub>OW</sub>) [1]
- activity coefficients [1, 2], solvation free energies [1], Henry's law constants [1],  $pK_a$  values [1]
- solubility [1, 2]
- vapor-liquid diagram binary mixture (VLE/LLE) [1, 2]



## COSMO RESULT FILES

COSMO-RS needs as input for the calculation so called COSMO result files for each compound, which are results of quantum mechanical calculation using COSMO. In ADF such a COSMO result file is called a TAPE21 (.t21) file or a COSKF file (.coskf). With MOPAC such a COSMO result file is a .cos file, which can be converted to a COSKF file. In other programs such a file can be a .cosmo file. ADF has a database of .coskf files, the COSMO-RS compound database *ADFCRS-2010* (page 15), and an ionic liquid database *ADFCRS-IL-2014* (page 16). At <http://www.design.che.vt.edu/VT-Databases.html> a database of .cosmo files can be found, which were made with a different program. Note that the optimal COSMO-RS parameters may depend on the program chosen.

### 3.1 ADF COSMO calculation

#### 3.1.1 ADF COSMO settings

Here it is described briefly how to make COSMO result files consistent with the way they were made for the ADF parametrization of COSMO-RS to ensure full parameter applicability. First a gas phase geometry optimization should be performed with ADF, with a small core TZP basis set, the Becke-Perdew functional, the relativistic scalar ZORA method, and good numerical integration quality:

```
BASIS
  type TZP
  core Small
  I ZORA/TZ2P/I.4p
END
XC
  GGA Becke Perdew
END
BeckeGrid
  Quality Good
End
relativistic scalar zora
```

For heavier elements than krypton (Z36), like iodine, a small core TZ2P basis set is required. The resulting TAPE21 of the molecule (rename it compound\_gasphase.t21) is used as a restart file in the COSMO calculation. The ADF COSMO calculation is performed with the following settings:

```
SYMMETRY NOSYM
SOLVATION
  Surf Delley
  Solvent name=CRS emp=0.0 cav0=0.0 cav1=0.0
  Charged method=CONJ corr
  C-Mat EXACT
  SCF VAR ALL
  RADII
```

```

H 1.30
C 2.00
N 1.83
O 1.72
F 1.72
Si 2.48
P 2.13
S 2.16
Cl 2.05
Br 2.16
I 2.32
SubEnd
END
XC
  GGA Becke Perdew
END
BeckeGrid
  Quality Good
End
relativistic scalar zora
RESTART compound_gasphase.t21

```

In this COSMO calculation the non-default Delley type of cavity construction is chosen (See Ref.[5 (page 51)] for details on the Delley surface construction). The name of the solvent is CRS, which sets the dielectric constant to infinite and sets the radius of the probing sphere to determine the solvent excluded part of the surface to 1.3 Angstrom.

In case of a cation or an anion, in both the gas phase calculations as well as in the COSMO calculation one should include the charge with the key CHARGE.

In the Radii subblock key the Klamt atomic cavity radii are chosen. The parameters emp, cav0, and cav1 are zero. The corr option to the CHARGED subkey constrains the computed solvent surface charges to add up to the negative of the molecular charge. Specifying exact for the C-MAT subkey causes ADF to compute straightforwardly the Coulomb potential due to the charge  $q$  in each point of the molecular numerical integration grid and integrate against the electronic charge density. This is, in principle, exact but may have inaccuracies when the numerical integration points are very close to the positions of a charge  $q$ . To remedy this, starting from ADF2010 the electrostatic potential is damped in case of (very) close lying numerical integration points and COSMO surface points. The numerical stability of the results compare to those of ADF2009 was increased as a result of this. Specifying exact for the C-MAT subkey also requires that the ADF calculation uses SYMMETRY NOSYM.

The resulting TAPE21 (rename it compound.t21) of the COSMO calculation is a COSMO result file.

In a COSMO-RS calculation only the 'COSMO' part of this file is needed. One can make a kf file compound.coskf, which only consists of the section 'COSMO' if one does:

```
$ADFBIN/cpkf compound.t21 compound.coskf "COSMO"
```

The file compound.coskf should not exist before this command is given. Note that such a .coskf file is not a complete TAPE21 anymore. For example, only the COSMO surface can be viewed with ADFview. It is useful mostly for COSMO-RS calculations.

**Links** COSMO-RS GUI tutorial: COSMO result files [1]

### 3.1.2 Atomic cation or anion

In case of an atomic calculation one should of course not perform a geometry optimization. In case of a cation or an anion, in both the gas phase calculations as well as in the COSMO calculation one should include the charge with the key CHARGE. Only for atomic calculations one should include the argument method=atom to the subkey Charged of the key SOLVATION:



```

SOLVATION
  Surf Delley
  Solvent name=CRS cav0=0.0 cav1=0.0
  Charged method=atom corr
  C-Mat EXACT
  SCF VAR ALL
END

```

### 3.1.3 Accuracy

Several parameters in the COSMO calculation can influence the accuracy of the result of the quantum mechanical calculation. Some of these parameters will be discussed. Note that if one chooses different parameters in the COSMO calculation one may also have to reparametrize the ADF COSMO-RS parameters. A list of some of the ADF COSMO parameters.

- XC functional
- basis set
- fit set
- atomic cavity radii and radius of the probing sphere
- cavity construction
- geometry

The atomic cavity radii and the radius of the probing sphere are the same as in Ref. [2 (page 51)], which describes the COSMO-RS method developed by Klamt et al., which is implemented in ADF. The Becke Perdew functional is relatively good for weakly bound systems, but may not be so good in other cases. The basis set TZP is a compromise basis set. For heavier elements than krypton (Z36), like iodine, a TZ2P basis set is required, including the relativistic scalar ZORA method. Since the relativistic method hardly cost extra time compared to a non-relativistic method, the scalar relativistic scalar ZORA method is recommended to be used also for light elements. The Delley type of cavity construction in ADF can give a large number of COSMO points. The XC functional, basis set, and cavity construction chosen in the ADF COSMO calculation have a similar accuracy as those that were used in Ref. [2 (page 51)]. Note that they are not exactly the same as were used in Ref. [2 (page 51)], since in that paper a different quantum mechanical program was used.

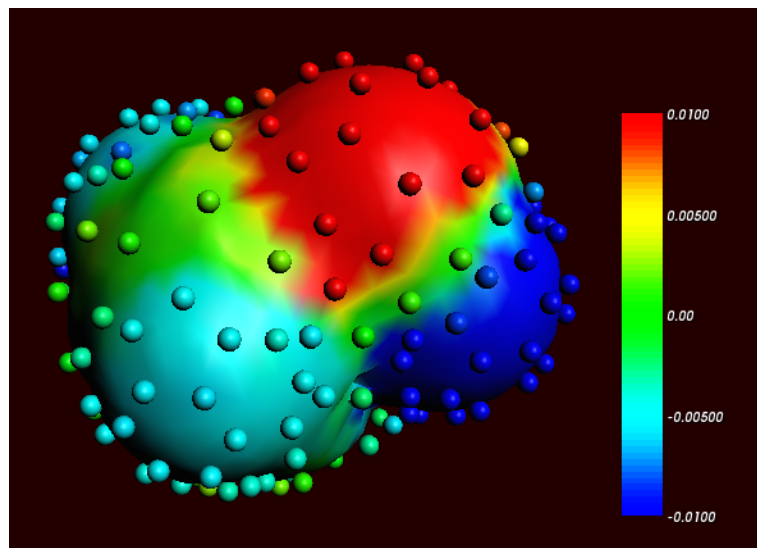
In the parametrization for ADF the same geometry was used for the gas phase and the COSMO calculation, which is different than in Ref. [2 (page 51)]. It depends on the actual solvent if reoptimizing the molecule in the COSMO calculation may give better results. Note that the dielectric medium used in the COSMO model has an infinite dielectric constant in the COSMO-RS model. Thus a geometry optimization of the molecule in the COSMO calculation might be more appropriate for a molecule dissolved in water than for a molecule dissolved in n-hexane.

The fit set in ADF is not always able to describe the Coulomb potential accurately at each of the COSMO surface points. In regular ADF calculations this problem is not apparent since the numerical errors in the integrals computed in the vicinity of the COSMO surface have little impact. However, in COSMO calculations this may have some effect. This is why the option C-Mat exact was selected above, instead of the default C-Mat pot option. Another possibility is to add more fit functions, for example, using the ADDDIFFUSEFITFUNCTIONS key in the input for the adf calculation.

### 3.1.4 Cavity construction

The Esurf type of cavity construction in ADF with default settings does not give a large number of COSMO points. Therefore it is recommended to use the so called Delley type of cavity construction (Ref.[5 (page 51)]), which allows one to construct a surface which has many more points. The Esurf type of cavity construction also allows many more points if one sets the option NFDiv of the subkey DIV of the key SOLVENT to a larger value than the default value

of 1. This will not be discussed here further. In ADF2010 the numerical stability of the Delley surface has been improved, by merging close lying COSMO surface points, and removing COSMO surface points with a small surface area. A figure of a COSMO surface with the Esurf type of cavity construction with default settings is given below. In this figure the small spheres represent the COSMO surface points that are used for the construction of the COSMO surface. The red part represents positive COSMO charge density, the blue part negative COSMO charge density (the coloring scheme is chosen to match the one by Klamt):

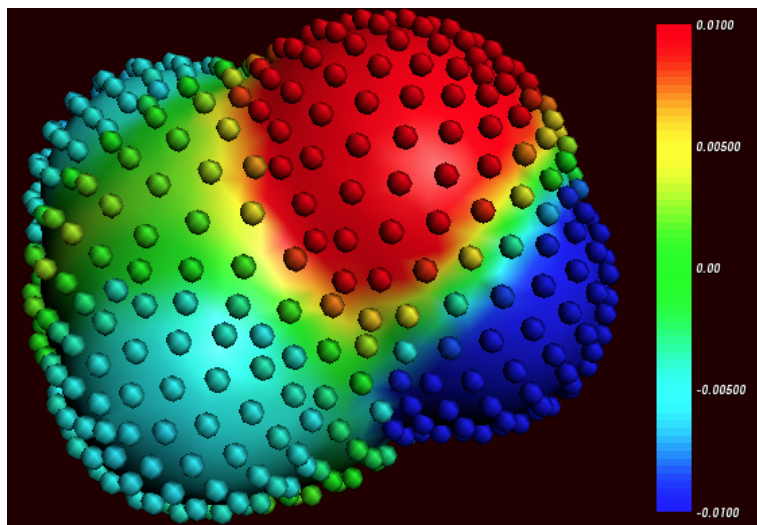


Cosmo charge density on the COSMO surface of methanol, Esurf surface (picture made with ADFview).

One can construct a surface which has many more points using a so called Delley surface. For the subkey SURF of the key SOLVENT one can choose delley. The subkey DIV of the key SOLVENT has extra options leb1 (default value 23), leb2 (default value 29), and rleb (default value 1.5 Angstrom). If the cavity radius of an atom is lower than rleb use leb1, otherwise use leb2. These values can be changed: using a higher value for leb1 and leb2 gives more surface points (maximal value leb1, leb2 is 29). A value of 23 means 194 surface points in case of a single atom, and 29 means 302 surface points in case of a single atom Typically one could use leb1 for the surface point of H, and leb2 for the surface points of other elements.

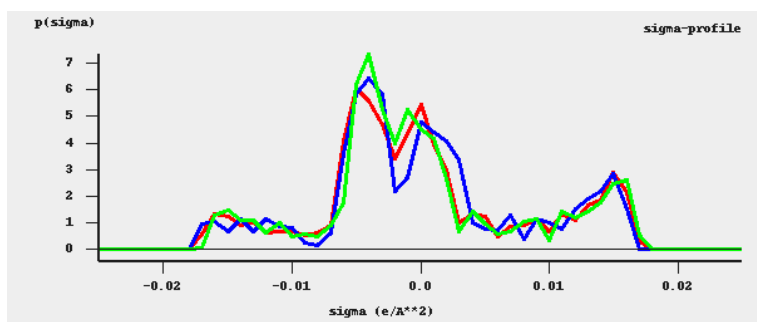
The next figure is made with the following (default for the Delley surface) settings:

```
SOLVATION
  SURF Delley
  DIV leb1=23 leb2=29 rleb=1.5
END
```



Cosmo charge density on the COSMO surface of methanol, Delley surface (picture made with ADFview).

The different ways of constructing the cavity has some consequences for the  $\sigma$ -profile of methanol, see the figure below:



$\sigma$ -profiles of methanol (picture made with the CRS-GUI). In this picture the blue line is the  $\sigma$ -profile with the Esurf type of construction, the red line is that with the Delley type of construction with many surface points. For comparison, the green line is the  $\sigma$ -profile of methanol if a large QZ4P basis set is used, again with the Delley type of construction with many surface points.

## 3.2 COSMO-RS Database ADFCRS-2010

The COSMO-RS Database ADFCRS-2010 contains 1892 compounds, mostly solvents and small molecules. This database consists of ADF COSMO result (.coskf) files, which are results of ADF quantum mechanical calculations using COSMO, with settings suitable for use in our COSMO-RS module. The geometries have been optimized with ADF. This database makes the COSMO-RS functionality much easier and faster (the time-consuming DFT step is already done ..) to use. Follow the COSMO-RS GUI Tutorial on the COSMO-RS compound database for more information on how to download and install the zipped COSMO-RS Database ADFCRS-2010 <http://downloads.scm.com/Downloads/crs/ADFCRS-2010.zip>, and how to use it.

The starting point for this database was a database of structures made by Prof. Sandler's group at the University of Delaware. The work of the Sandler group is based in part on earlier work by the group of Prof. Liu at Virginia Technical University, reported in these papers:

Mullins, E.; Oldland, R.; Liu, Y.A.; Wang, S.; Sandler, S.I.; Chen, C.-C.; Zwolak, M.; Seavey, K.C. *Sigma-Profile Database for Using COSMO-Based Thermodynamic Methods*. *Ind. Eng. Chem. Res.* 2006, 45 (12), 4389-4415. (<http://pubs.acs.org/doi/abs/10.1021/ie060370h>)

Mullins, E.; Liu, Y.A.; Ghaderi, A.; Fast, S.D. *Sigma Profile Database for Predicting Solid Solubility in Pure and Mixed Solvent Mixtures for Organic Pharmacological Compounds with COSMO-Based Thermodynamic Methods*. *Ind. Eng. Chem. Res.* 2008, 47 (5), 1707-1725. (<http://pubs.acs.org/doi/abs/10.1021/ie0711022>)

Phillips, K.L.; Sandler, S.I.; Greene, R.W.; Di Toro, D.M. *Quantum Mechanical Predictions of the Henry's Law Constants and Their Temperature Dependence for the 209 Polychlorinated Biphenyl Congeners*. *Environ. Sci. Technol.* 2008, 42 (22), 8412-8418. (<http://pubs.acs.org/doi/abs/10.1021/es800876w>)

All structures in the database ADFCRS-2010 differ from those in the papers above, as they are the result of ADF geometry optimizations.

The database contains CAS Registry Numbers. CAS Registry Number is a Registered Trademark of the American Chemical Society.

### 3.3 COSMO-RS Ionic Liquid Database ADFCRS-IL-2014

Ionic liquids (ILs), usually consisting of a large organic cation and a small inorganic polyatomic anion, have attracted considerable attention in recent years due to their unique thermophysical properties. The low vapor pressure and high conductivity of these molten salts combined with highly tunable properties, have resulted in highly diverse applications across many different fields in chemistry, materials science (battery electrolytes), chemical engineering (gas sorption and purification), and many more.

The COSMO-RS ionic liquid database ADFCRS-IL-2014 contains 80 cations and 56 anions. This ADFCRS-IL-2014 database consists of ADF COSMO result (.coskf) files, from standard ADF quantum mechanical calculations, as described in COSMO-RS GUI Tutorial: COSMO result files. Follow the COSMO-RS GUI Tutorial on Ionic Liquids for more information on how to download and install the zipped COSMO-RS Ionic Liquid Database ADFCRS-IL-2014 <http://downloads.scm.com/Downloads/crs/ADFCRS-IL-2014.zip>, and how to use it.

SCM gratefully acknowledges Prof. Zhigang Lei's research group (State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, China) for providing the ionic liquid database as well as the corresponding tutorial.

The work of Zhigang Lei group based on the COSMO-RS model using the ADF software is listed as follows:

Z.Lei, C. Dai, J. Zhu, B. Chen, *Extractive distillation with ionic liquids: A review*, *AIChE Journal* 60, 3312 (2014) (<http://dx.doi.org/10.1002/aic.14537>)

Z.Lei, C. Dai, B. Chen, *Gas solubility in ionic liquids*, *Chemical Reviews* 14, 1289 (2014) (<http://dx.doi.org/10.1021/cr300497a>)

Z.Lei, J. Han, Q. Li, and B. Chen, *Process Intensification on the Supercritical Carbon Dioxide Extraction of Low-Concentration Ethanol from Aqueous Solutions*, *Industrial Engineering Chemistry research* 51, 2730 (2012) (<http://dx.doi.org/10.1021/ie2021027>)

Z.Lei, J. Han, B. Zhang, Q. Li, J. Zhu, and B. Chen, *Solubility of CO<sub>2</sub> in Binary Mixtures of Room-Temperature Ionic Liquids at High Pressures*, *Journal of Chemical Engineering data* 57, 2153 (2012) (<http://dx.doi.org/10.1021/je300016q>)

Z.Lei, C. Dai, X. Liu, L. Xiao, and B. Chen, *Extension of the UNIFAC Model for Ionic Liquids*, *Industrial Engineering Chemistry research* 51, 12135 (2012) (<http://dx.doi.org/10.1021/ie301159v>)

Z.Lei, C. Dai, Q. Yang, J. Zhu, and B. Chen, *UNIFAC model for ionic liquid-CO (H<sub>2</sub>) systems: An experimental and modeling study on gas solubility*, *AIChE Journal* (2014), DOI: 10.1002/aic.14606 (<http://dx.doi.org/10.1002/aic.14606>)

### 3.4 MOPAC COSMO calculation

Here it is described briefly how to make MOPAC COSMO result files.

The simplest way is to use ADFinput. Draw the molecule using ADFinput, and save the .adf file. Select **Right Panel** → **MOPAC** → **Solvation method** → **COSMO-CRS**. Press Run to run the MOPAC calculation. A .coskf file will be saved that can be used as input in COSMO-RS calculations.

Technically ADFinput will add some keywords to the input for MOPAC (see also <http://www.openmopac.net>). The main input keys for MOPAC that are used are:

```
PM6 EPS=9999.9 RSOLV=1.3 COSWRT NSPA=362
```

The use of COSWRT makes MOPAC create a .cos file, which is converted to a .coskf file by \$ADFBIN/cosmo2kf

```
cosmo2kf file.cos file.coskf
```

Note that this is automatically done if one uses ADFinput.

Compared to the default ADF COSMO-RS values a few *COSMO-RS parameters* (page 19) were reoptimized for MOPAC PM6 COSMO result files to improve the calculation of a number of partition coefficients, when compared to experimental values. Note that MOPAC is a semi-empirical quantum chemistry program, whereas ADF is based on density functional theory (DFT). Thus the MOPAC COSMO result files will not be of the same quality as the ADF COSMO result files.



## THE COSMO-RS PROGRAM

The ADF COSMO-RS command line program *crs* is described here, including all input options.

### 4.1 Running the COSMO-RS program

Running the COSMO-RS program involves the following steps:

- Construct an ASCII input file, say *in*.
- Run the program by typing (under UNIX): `$ADFBIN/crs < in > out`
- Move / copy relevant result files (in particular *CRSKF*) to the directory where you want to save them, and give them appropriate names.
- Inspect the standard output file *out* to verify that all has gone well.

Note that in the one can also put the call to `$ADFBIN/crs` inside a script, which could be named, for example, 'example.run'. Such shell script 'example.run' needs be executable, if it isn't you will need to make it executable, e.g. `chmod u+x example.run`. The 'example.run' file needs to be executed as a shell script, not as input to `$ADFBIN/crs`.

### 4.2 COSMO-RS and COSMO-SAC parameters

The COSMO-RS model has general parameters and element specific parameters. ADF's COSMO-SAC 2013-ADF model has general parameters, but also uses some of the COSMO-RS parameters, such as the element specific parameters. There are also technical and accuracy parameters, such as convergence criteria. This section explains how to set these parameters, and shows the default values for these parameters. By default the COSMO-RS method is chosen.

#### 4.2.1 COSMO-RS general parameters

```
CRSPARAMETERS
{RAV          rav}
{APRIME       aprime}
{FCORR        fcorr}
{CHB          chb}
{SIGMAHBOND   sigmahbond}
{AEFF         aeff}
{LAMBDA       lambda}
{OMEGA        omega}
{ETA          eta}
{CHORTF       chortf}
```

```
{combi1998 | combi2005}
{hb_all | hb_hnof}
{hb_temp | hb_notemp}
{fast | nofast}
End
```

The ADF default values are optimized parameters for ADF calculations. The Klamt values can be found in Ref. [2 (page 51)]. See also Ref. [2 (page 51)] for the meaning of the parameters.

symbol	ADF Default	ADF combi1998	Klamt	MOPAC PM6
	Ref. [4 (page 51)]	Ref. [4 (page 51)]	Ref. [2 (page 51)]	
rav ( $r_{av}$ )	0.400	0.415	0.5	0.400
aprime (a')	1510.0	1515.0	1288.0	1550.0
fcorr ( $f_{corr}$ )	2.802	2.812	2.4	2.802
chb ( $c_{hb}$ )	8850.0	8850.0	7400.0	8400.0
sigmahbond ( $\sigma_{hb}$ )	0.00854	0.00849	0.0082	0.00978
aeff ( $a_{eff}$ )	6.94	7.62	7.1	5.96
lambda ( $\lambda$ )	0.130	0.129	0.14	0.135
omega ( $\omega$ )	-0.212	-0.217	-0.21	-0.212
eta ( $\eta$ )	-9.65	-9.91	-9.15	-9.65
chortf ( $c^\perp$ )	0.816	0.816	0.816	0.816
combi1998   combi2005	combi2005	combi1998	combi1998	combi2005
hb_all   hb_hnof	hb_hnof	hb_hnof	hb_hnof	hb_hnof
hb_temp   hb_notemp	hb_temp	hb_notemp	hb_notemp	hb_temp
fast   nofast	fast	fast	fast	fast

**chortf** See Ref. [2 (page 51)] for the definitions:  $\sigma_v^\perp = \sigma_v^0 - c^\perp \sigma_v$

**combi1998 | combi2005** If the subkey combi1998 is included a thermodynamically inconsistent combinatorial contribution to the chemical potential  $\mu_i^{comb}$  of Ref.[2 (page 51)] is used. If the subkey combi2005 is included (default) a thermodynamically consistent combinatorial contribution of Ref.[3 (page 51)] is used. See [the section on the combinatorial term](#) (page 5) and Ref.[3 (page 51)].

**hb\_all | hb\_hnof** If the subkey hb\_all is included hydrogen bond interaction can be included between segments that belong to H atoms and all other segments. If the subkey hb\_hnof is included (default) hydrogen bond interaction can be included only between segments that belong to H atoms that are bonded to N, O, or, F, and segments that belong to N, O, or F atoms.

**hb\_temp | hb\_notemp** If the subkey hb\_notemp is included the hydrogen bond interaction is not temperature dependent, as in Ref.[2 (page 51)]. If the subkey hb\_temp is included (default) the hydrogen bond interaction is temperature dependent, as in Ref.[3 (page 51)]. See [the section on the temperature dependent hydrogen bond interaction](#) (page 6) and Ref.[3 (page 51)].

**fast | nofast** If the subkey fast is included the fast approximation is used. This fast approximation is the default. Use nofast for the original approach. See [the section on the fast approximation for COSMO-RS calculations](#) (page 5).

**Links** COSMO-RS GUI tutorial: set COSMO-RS parameters [1]

## 4.2.2 COSMO-RS element specific parameters

```
DISPERSION
{H dispH}
{C dispC}
{N dispN}
```



```
{ ... }
End
```

The following table gives the element specific dispersion constants. The ADF default values are optimized parameters for ADF calculations. The Klamt values can again be found in Ref. [2 (page 51)]. The constants for F, Si, P, S, Br, and I in the ADF defaults were only fitted to a small number of experimental values or taken from Ref. [3 (page 51)].

element	ADF Default	ADF combi1998	Klamt
			Ref. [2 (page 51)]
H	-0.0340	-0.0346	-0.041
C	-0.0356	-0.0356	-0.037
N	-0.0224	-0.0225	-0.027
O	-0.0333	-0.0322	-0.042
Cl	-0.0485	-0.0487	-0.052
F	-0.026		
Si	-0.04		
P	-0.045		
S	-0.052		
Br	-0.055		
I	-0.062		

Note that not for all elements in the periodic system COSMO-RS parameters were fitted.

**Links** COSMO-RS GUI tutorial: set COSMO-RS parameters [1]

### 4.2.3 COSMO-SAC general parameters

The ADF COSMO-RS program can calculate activity coefficients using the COSMO-SAC 2013-ADF model, based on Ref. [9 (page 51)]. Like in the COSMO-RS method, pure compound vapor pressures can be given as input, for example, if experimental values are available. If these values are not specified then the pure compound vapor pressure will be calculated according to the COSMO-SAC 2013-ADF model. This part of the COSMO-SAC 2013-ADF has been implemented in ADF2016. The COSMO-SAC 2013-ADF parameters in Ref. [9 (page 51)] are optimized parameters for use with ADF COSMO result files. Note that earlier COSMO-SAC methods [6,7 (page 51)] do not have parameters that were optimized for use with ADF COSMO result files. The key COSMOSAC2013 needs to be included if one wants to do a COSMO-SAC 2013-ADF calculation. For earlier COSMO-SAC methods one needs to include the key COSMOSAC.

```
COSMOSAC2013 | COSMOSAC
SACPARAMETERS
{AEFF      aeff}
{FDECAY    fdecay}
{SIGMA0    sigma0}
{RN        rn}
{QN        qn}
{AES       aes}
{BES       bes}
{COHOH     cohoh}
{COTOT     cotot}
{COHOT     cohoh}
{RAV       rav}
{QS        qs}
{hb_temp   | hb_notemp}
End
```

symbol	2013-ADF Xiong	2010 Hsieh	2007 Wang
	Ref. [9 (page 51)]	Ref. [7 (page 51)]	Ref. [6 (page 51)]
a <sub>eff</sub> (a <sub>eff</sub> )	6.4813	7.25	7.25
f <sub>decay</sub> (f <sub>decay</sub> )	-	3.57	3.57
sigma0 (σ <sub>0</sub> )	0.01233	0.007	0.007
rn (r)	-	66.69	66.69
qn (q)	79.352	79.53	79.53
a <sub>ES</sub> (A <sub>ES</sub> )	7877.13	6525.69	8451.77
b <sub>ES</sub> (B <sub>ES</sub> )	0.0	1.4859 10 <sup>8</sup>	0.00
c <sub>OH-OH</sub> (c <sub>OH-OH</sub> )	5786.72	4013.78	3484.42
c <sub>OT-OT</sub> (c <sub>OT-OT</sub> )	2739.58	932.31	3484.42
c <sub>OH-OT</sub> (c <sub>OH-OT</sub> )	4707.75	3016.43	3484.42
r <sub>av</sub> (r <sub>av</sub> )	0.51	-	-
q <sub>s</sub> (q <sub>s</sub> )	0.57	-	-
hb_temp   hb_notemp	hb_notemp	hb_notemp	hb_notemp

See also Refs. [7,9 (page 51)] for the meaning of the parameters a<sub>eff</sub>, f<sub>decay</sub>, σ<sub>0</sub>, r, q, A<sub>ES</sub>, B<sub>ES</sub>, c<sub>OH-OH</sub>, c<sub>OT-OT</sub>, c<sub>OH-OT</sub>, r<sub>av</sub>, q<sub>s</sub>. The parameter names in [6 (page 51)] have been translated into parameter names used in Ref. [7 (page 51)], by calculating A<sub>ES</sub> from 0.3 f<sub>pol</sub> a<sub>eff</sub><sup>3/2</sup> / (2ε<sub>0</sub>), using B<sub>ES</sub> = 0, and using c<sub>OH-OH</sub> = c<sub>OT-OT</sub> = c<sub>OH-OT</sub> = c<sub>hb</sub>. The parameters f<sub>decay</sub> and r are not used in COSMO-SAC 2013-ADF [9 (page 51)]. The parameters r<sub>av</sub> and q<sub>s</sub> are not used in earlier COSMO-SAC methods [6,7 (page 51)]. The element specific COSMO-SAC 2013-ADF epsilon constants can be set with the block key *EPSILON* (page 22). These element specific epsilon constants can not be used in ADF's implementation of earlier COSMO-SAC methods.

**hb\_temp | hb\_notemp** If the subkey hb\_notemp is included (default) the hydrogen bond interaction is not temperature dependent, as in Refs. [6,7,9 (page 51)]. If the subkey hb\_temp is included the temperature dependence of the hydrogen bond interaction f<sub>hb</sub>(T) is the same as is described in *the section on the temperature dependent hydrogen bond interaction* (page 6).

For older COSMO-SAC methods some COSMO-RS specific parameters are used:

```

COSMOSAC
SACPARAMETERS
...
{OMEGA      omega}
{ETA        eta}
End
    
```

symbol	2010 Hsieh	2007 Wang
	Ref. [7 (page 51)]	Ref. [6 (page 51)]
omega (ω)	-0.212	-0.212
eta (η)	-9.00	-9.00

In ADF2016 these parameters are not used in the COSMO-SAC 2013-ADF method, only in the ADF implementation of the older COSMO-SAC methods. The parameters ω, η and the element specific COSMO-RS dispersion constants are taken from the COSMO-RS model. The element specific COSMO-RS dispersion constants can be set with the block key *DISPERSION*. ω, η, and the element specific COSMO-RS dispersion constants are used in a COSMO-RS like method for the calculation of pure compound vapor pressures.

#### 4.2.4 COSMO-SAC element specific parameters

```

COSMOSAC2013
EPSILON
{H  epsH}
{C  epsC}
{N  epsN}
    
```

```
{...}
End
```

The following table gives the element specific epsilon constants in case of COSMO-SAC 2013-ADF, see Ref. [9 (page 51)]. Like in the COSMO-RS method, pure compound vapor pressures can be given as input, for example, if experimental values are available. In these values are not given, in ADF2016 the pure compound vapor pressure will be approximated using the the COSMO-SAC 2013-ADF method, which depend on these element specific epsilon constants. These constants will also have an effect on the calculated activity coefficients in case of a mixture. Note that these only have an effect in the ADF's COSMO-SAC 2013-ADF implementation.

element	2013-ADF Xiong Ref.[9 (page 51)]
H	338.13
C.sp3	29160.92
C.sp2	30951.83
C.sp	20685.98
N.sp3	23488.54
N.sp2	22663.34
N.sp	6390.40
O.sp3-H	8527.06
O.sp3	8484.38
O.sp2	6736.85
O.sp2-N	12145.28
Cl	8435.13
F	82512.21
P	56067.81
S	45065.19
Br	62947.83
I	105910.88

Note that not for all elements in the periodic system COSMO-SAC 2013-ADF parameters were fitted.

If one leaves the EPSILON block keyword empty the contribution of the mixture dispersion to the activity coefficient will be zero.

```
EPSILON
End
```

**Links** COSMO-RS GUI tutorial: Expert option: set COSMO-SAC 2013-ADF parameters [1]

#### 4.2.5 Technical and accuracy parameters

```
TECHNICAL
{RSCONV rsconv}
{SACCONV sacconv}
{MAXITER maxiter}
{BPCONV bpconv}
{BPMAXITER bpmaxiter}
{SOLCONV solconv}
{SOLMAXITER solmaxiter}
{SOLXILARGE solxilarge}
{EHDELTAAT ehdeltaAT}
End
```

symbol	Default values
rsconv	10 <sup>-7</sup> kcal/mol
sacconv	10 <sup>-7</sup>
maxiter	10000
bpconv	10 <sup>-6</sup> bar
bpmaxiter	40
solconv	10 <sup>-5</sup> molar fraction
solmaxiter	40
solxilarge	0.99 molar fraction
ehdeltaT	1.0 Kelvin

**rsconv** Convergence criterion in kcal/mol in chemical potential calculation, not used in COSMO-SAC 2013-ADF. Default value 1e-7 kcal/mol.

**sacconv** Convergence criterion in activity coefficient calculation, only used in COSMO-SAC 2013-ADF. Default value 1e-7.

**maxiter** Maximum number of cycles in chemical potential or activity coefficients calculation. Default value 10000.

**bpconv** Convergence criterion (bar) for isobar or solvent boiling point calculation. Default value 1e-6 bar.

**bpmaxiter** Maximum number of cycles in isobar or solvent boiling point calculation. Default value 40.

**solconv** Convergence criterion (molar fraction) used in solubility calculations. Default value 1e-5 molar fraction.

**solmaxiter** Maximum number of cycles in solubility calculation. Default value 40.

**solxilarge** Threshold for (im-)miscibility (molar fraction) in solubility calculations. Above this value the mixture is considered to be fully miscible. Default value 0.99.

**ehdeltaT**  $\Delta T$  (Kelvin) used in the calculation of the excess enthalpy using the Gibbs-Helmholtz equation and in the calculation of the enthalpy of vaporization using the Clausius-Clapeyron equation using a numerical derivative with respect to T. Default value 1.0 Kelvin.

**Links** COSMO-RS GUI tutorial: set COSMO-RS or COSMO-SAC 2013-ADF parameters [1]

## 4.3 Compounds

For each compound one has to add the keyword COMPOUND

```

COMPOUND filename
{cosmofile}
{drophbond}
{NRING nring}
{FRAC1 frac1}
{FRAC2 frac2}
{PVAP pvap}
{TVAP tvap}
{Antoine A B C}
{MELTINGPOINT meltingpoint}
{HFUSION hfusion}
{CPFUSION cpfusion}
{FLASHPOINT flashpoint}
{DENSITY density}
{SCALEAREA scalearea}
End

```

**filename** The filename (can be a full path, otherwise relative path is assumed) should be a COSMO result file. How to make an ADF COSMO result file can be found [here](#) (page 9).

**cosmofile** If the subkey cosmofile is included the file should be an ASCII COSMO file (.cosmo). If not specified (default) the file should be a kf file, either an ADF COSMO result file TAPE21 (.t21) or a COSKF file (.coskf).

**drophbond** If the subkey drophbond is included no hydrogen-bond terms will be included for this compound. If not specified (default) the hydrogen-bond terms are included for this compound.

**nring** The number of ring atoms. This is a COSMO-RS parameter. It should be 6 for benzene, for example. Default value is 0.

**frac1** The molar fraction of the compound in the solvent (mass fraction if the key MASSFRACTION is used). This is solvent 1 in case of the calculation of partition coefficients (Log P) or in case of a composition line.

**frac2** The molar fraction of solvent 2 (mass fraction if the key MASSFRACTION is used), only used in case of the calculation of partition coefficients (Log P) or in case of a composition line.

**pvap, tvap** Pure compound vapor pressure pvap (bar) at temperature tvap (Kelvin). Used only if both pvap and tvap are specified, and then will have an effect on the calculated vapor pressures or boiling points. Alternative is to set the Antoine coefficients. If both are not specified the pure compound vapor pressure is approximated using the COSMO-RS method.

**A, B, C** A, B, and C are the pure compound Antoine coefficients, such that:  $\log P = A - B/(T+C)$ . This Antoine equation is a 3-parameter fit to experimental pure compound vapor pressures P (bar) over a restricted temperature T (Kelvin) range. If the Antoine coefficients are specified this will have an effect on the calculated vapor pressures or boiling points. Alternative is to give input values for the pure compound vapor pressure at a fixed temperature. If both are not specified the pure compound vapor pressure is approximated using the COSMO-RS method.

**meltingpoint, hfusion, cpfusion** Pure compound melting point meltingpoint (Kelvin), pure compound enthalpy of fusion hfusion (kcal/mol), and pure compound heat capacity of fusion cpfusion (kcal/(mol K)). Only used if both meltingpoint and hfusion are specified (cpfusion optional), and will then have an effect in solubility calculations if the temperature of the solvent is below the melting point.

**flashpoint** Pure compound flash point flashpoint (Kelvin).

**density** Pure compound density density (kg/L). Used for calculating the volume of a solvent molecule.

**scalearea** Input scaling of COSMO surface area for a given compound. Default value 1.0 means the COSMO surface area is not scaled. Changing this value is an expert option, for example, to fit to experiment.

**Links** COSMO-RS GUI tutorial: set pure compound parameters [1]

## 4.4 Temperature

```
TEMPERATURE temperature {temperature_high ntemp}
```

**temperature** Temperature (Kelvin) at which temperature the COSMO-RS calculation should take place. Default room temperature 298.15. The first temperature in case of a range of temperatures.

**temperature\_high** The last temperature (Kelvin) in case of a range of temperatures. Only used in case of solvent vapor pressure calculations or solubility calculations.

**ntemp** The number of temperatures in case of a range of temperatures.

## 4.5 Pressure

```
PRESSURE pressure {pressure_high npress}
```

**pressure** Pressure (bar) at which pressure the COSMO-RS calculation should take place. Default 1.01325 bar (1 atm). The first pressure in case of a range of pressures.

**pressure\_high** The last pressure (bar) in case of a range of pressures. Only used in case of solvent boiling point calculations.

**npress** The number of pressures in case of a range of pressures.

## 4.6 Molar fractions and mass fraction

By default the ADF COSMO-RS program assumes molar fractions as input. This can be changed into mass fractions if one includes:

```
MASSFRACTION
```

## 4.7 Properties

### 4.7.1 Vapor pressure

The vapor pressure of a mixture can be calculated with:

```
PROPERTY vaporpressure  
End
```

In case of a mixture the mole fraction of each compound of the solvent should be given with the subkey FRAC1 of the key COMPOUND for each compound. In case of a mixture also activity coefficients, and excess energies are calculated.

To calculate pure compound vapor pressures for more than one compound use:

```
PROPERTY purevaporpressure  
End
```

It is possible to calculate the vapor pressure for a temperature range, see key TEMPERATURE.

The input pure compound vapor pressure will be used in the calculation of the vapor pressure of this compound if it is supplied with the key COMPOUND for this compound. If it is not specified then it will be approximated using the COSMO-RS method.

**Links** COSMO-RS GUI tutorial: solvent vapor pressure [1, 2]

### 4.7.2 Boiling point

The boiling point of a mixture can be calculated with the block key:

```
PROPERTY boilingpoint  
End
```

In case of a mixture the mole fraction of each compound of the solvent should be given with the subkey FRAC1 of the key COMPOUND for each compound. In case of a mixture also activity coefficients, and excess energies are calculated.

To calculate pure compound boiling points for more than one compound use:

```
PROPERTY pureboilingpoint
End
```

It is possible to calculate the boiling temperature for a pressure range, see key PRESSURE.

The input pure compound vapor pressure will be used in the calculation of the vapor pressure of this compound in the mixture if it is supplied with the key COMPOUND for this compound. If it is not specified then it will be approximated using the COSMO-RS method.

The COSMO-RS calculation of the boiling temperature of a solvent is performed with an iterative method. The temperature is varied until the calculated vapor pressure is within a certain threshold of the desired pressure.

**Links** COSMO-RS GUI tutorial: boiling point of a solvent [1]

### 4.7.3 Solvent flash point

The flash point (lower flammable limit) of a compound is the lowest temperature at which the vapor of the compound forms an ignitable mixture in air. The COSMO-RS module can calculate the flash point of a mixture. The COSMO-RS module, however, does not calculate or predict the flash point of pure compounds. The COSMO-RS method is used to calculate the partial vapor pressures of each compound in the mixture, and it uses Le Chatelier's mixing rule to calculate the flash point of this mixture in the gas phase. Input pure compound flash points should be provided by the user, with the subkey FLASHPOINT flashpoint of the key COMPOUND.

```
PROPERTY flashpoint
End
```

The mole fraction of each compound of the solvent should be given with the subkey FRAC1 of the key COMPOUND for each compound.

### 4.7.4 Partition coefficients (LogP)

The partition coefficient of a compound in a mixture of two immiscible solvents, can be calculated with:

```
PROPERTY logp
{VOLUMEQUOTIENT volumequotient}
End
```

**volumequotient** If the subkey VOLUMEQUOTIENT is included the volumequotient will be used for quotient of the molar volumes of solvent 1 and solvent 2 instead of calculated values.

The mole fraction of each compound of the solvent 1 and solvent 2 should be given with the subkey FRAC1 and subkey FRAC2 of the key COMPOUND for each compound, respectively. In case of partly miscible liquids, like, for example, the Octanol-rich phase of Octanol and Water, both components have nonzero mole fractions. The compounds that are included without a given mole fraction are considered to be infinite diluted solutes. The partition coefficients are calculated for all compounds.

One can use some compounds that are present in \$ADFHOME/atomicdata/ADFCRS (Water, 1-Octanol, Benzene, Ethoxyethane, Hexane), or one can use compounds from the ADFCRS-2010 database. For example, for Octanol/Water partition coefficients one can use:

```
Property logp
  VolumeQuotient 4.93
End
Compound "$ADFHOME/atomicdata/ADFCRS/1-Octanol.coskf"
  frac1 0.725
End
Compound "$ADFHOME/atomicdata/ADFCRS/Water.coskf"
```

```
frac1 0.275
frac2 1.0
End
```

**Links** COSMO-RS GUI tutorial: partition coefficients (log P) [1, 2], Octanol-Water partition coefficients (log P<sub>OW</sub>) [1]

### 4.7.5 Activity coefficients solvent and solute

The mole fraction of each compound of the solvent should be given with the subkey FRAC1 of the key COMPOUND for each compound. The compounds that are included without a given mole fraction are considered to be infinite diluted solutes. The activity coefficients are calculated for all compounds.

```
PROPERTY activitycoef
{DENSITYSOLVENT densitysolvent}
End
```

**densitysolvent** If the subkey DENSITYSOLVENT is included the densitysolvent will be used for the density of the solvent (kg/L) instead of calculated values. Relevant for the calculation of the Henry's law constant.

The input pure compound vapor pressure will be used in the calculation of the partial vapor pressure of this compound in the mixture if it is supplied with the key COMPOUND for this compound. If it is not specified then it will be approximated using the COSMO-RS method. Relevant for the calculation of the Henry's law constant.

The Henry's law constants are calculated in 2 units. The Henry's law constant  $k_H$  is the ratio between the liquid phase concentration of a compound and its partial vapor pressure in the gas phase. The dimensionless Henry's law constant  $k_H^{cc}$  is the ratio between the liquid phase concentration of a compound and its gas phase concentration.

Also calculated is  $\Delta G_{solv}^{liq-solv}$ , which is the solvation Gibbs free energy from the pure compound liquid phase to the solvated phase, and  $\Delta G_{solv}^{gas-solv}$ , which is the solvation Gibbs free energy from the pure compound gas phase to the solvated phase, with a reference state of 1 mol/L in both phases. In addition a Gibbs free energy is calculated which is the free energy of the solvated compound with respect to the gas phase energy of the spin restricted spherical averaged neutral atoms, the compound consist of. Note that zero-point vibrational energies are not taken into account in the calculation of this free energy. This energy could be used in the calculation of  $pK_a$  values.

**Links** COSMO-RS GUI tutorial: activity coefficients [1, 2], solvation free energies [1], Henry's law constants [1],  $pK_a$  values [1]

### 4.7.6 Solubility

The solubility of solutes in 1 mixture can be calculated with:

```
PROPERTY solubility
End
```

The mole fraction of each compound of the solvent should be given with the subkey FRAC1 of the key COMPOUND for each compound, and should add up to 1.0. The solutes should have zero molar fraction in the solvent. The solubility of 1 solute in pure solvents can be calculated with

```
PROPERTY puresolubility
End
```

The mole fraction of each pure solvent should be 1.0, and should be set the subkey FRAC1 of the key COMPOUND for each compound. The solute should have zero molar fraction in the solvent. It is possible to calculate the solubility of a solute at a temperature range, see key TEMPERATURE.



For solubility calculations of a solid compound one should add the pure compound melting point  $T_m$ , pure compound enthalpy of fusion  $\Delta H_{fus}$ , and optionally the pure compound heat capacity of fusion  $\Delta C_p$  using the subkeys `melt-point`, `hfusion`, and `cpfusion`, respectively, of the key `COMPOUND` for this compound. The COSMO-RS method does not predict these  $\Delta H_{fus}$ ,  $\Delta C_p$ , or  $T_m$ .

The assumption made in the solubility calculation may be invalid in case of a solubility of a liquid in a solvent, especially if the solubility of the solvent in the liquid is high. For binary systems one may check this by calculating the miscibility gap in the binary mixture of the two liquids. It is possible to calculate the solubility of a gas in a solvent, if one adds the subkey `isobar` and adds the partial vapor pressure `partialvaporpressure` (bar) of the gas as argument for the key `PRESSURE`:

```
PROPERTY solubility
  isobar
End

PRESSURE partialvaporpressure
```

The solubility of a gas in a solvent can also be calculated using Henry's law, which is valid for ideal dilute solutions, see the key `PROPERTY activitycoef`. The COSMO-RS calculation of the solubility of a compound is performed with an iterative method, since the activity coefficient of the compound depends on the molar fraction of this compound.

**Links** COSMO-RS GUI tutorial: solubility [1, 2]

#### 4.7.7 Binary mixture (VLE/LLE)

The COSMO-RS module can automatically calculate properties of a binary mixture, by calculating these properties for a number of different compositions.

Exactly two compounds should be given in the input file.

```
PROPERTY binmixcoef
{Nfrac nfrac}
{isotherm | isobar | flashpoint}
End
```

**nfrac** Number of different mixtures for which the binary mixture is calculated will be `nfrac+5`. Default value for `nfrac` is 10, which means 15 different mixtures.

**isotherm | isobar | flashpoint** If the subkey `isotherm` is included (default) the binary mixture will be calculated at a fixed temperature. If the subkey `isobar` is included the binary mixture will be calculated at a fixed vapor pressure. If the subkey `flashpoint` is included the flash point of the binary mixture will be calculated.

The input pure compound vapor pressure will be used in the calculation of the partial vapor pressure of this compound in the mixture if it is supplied with the key `COMPOUND` for this compound. If it is not specified then it will be approximated using the COSMO-RS method.

In case of a miscibility gap (LLE) data of the 2 immiscible liquid phases will be calculated. Also information about possible azeotropes will be calculated. With the COSMO-RS GUI, activity coefficients, (partial) vapor pressures, and excess energies can be viewed.

**Links** COSMO-RS GUI tutorial: vapor-liquid diagram binary mixture (VLE/LLE) [1, 2]

#### 4.7.8 Ternary mixture (VLE/LLE)

The COSMO-RS module can automatically calculate properties of a ternary mixture, by calculating these properties for a number of different compositions. Exactly three compounds should be given in the input file.

```
PROPERTY ternarymix
  {Nfrac nfrac}
  {isotherm | isobar | flashpoint}
End
```

**nfrac** Number of different mixtures for which the ternary mixture is calculated will be  $(nfrac+1)*(nfrac+2)/2$ . Default value for nfrac is 10, which means 55 different mixtures.

**isotherm | isobar | flashpoint** If the subkey isotherm is included (default) the ternary mixture will be calculated at a fixed temperature. If the subkey isobar is included the ternary mixture will be calculated at a fixed vapor pressure. If the subkey flashpoint is included the flash point of the ternary mixture will be calculated.

The input pure compound vapor pressure will be used in the calculation of the partial vapor pressure of this compound in the mixture if it is supplied with the key COMPOUND for this compound. If it is not specified then it will be approximated using the COSMO-RS method.

In case of a miscibility gap liquid-liquid equilibrium (LLE) data such as tie lines and an approximate phase diagram, are calculated. With the COSMO-RS GUI, activity coefficients, (partial) vapor pressures, and excess energies can be viewed as a colormap in a 2-dimensional plot with 2 of the liquid compositions on the axes.

**Links** COSMO-RS GUI tutorial: ternary mixtures (VLE/LLE) [1]

## 4.7.9 Solvents s1 - s2 Composition Line

The COSMO-RS module can linear interpolate between the compositions of solvent 1 and solvent 2, which both could be mixtures, and calculate properties, like activity coefficients, and excess energies. This property calculation does not calculate a possible miscibility gap. The mole fraction of each compound of the solvent 1 and solvent 2 should be given with the subkey FRAC1 and subkey FRAC2 of the key COMPOUND for each compound, respectively.

```
PROPERTY compositionline
  {Nfrac nfrac}
  {isotherm | isobar | flashpoint}
End
```

**nfrac** Number of different mixtures of the 2 solvents is calculated will be  $(nfrac+1)$ . Default value for nfrac is 10, which means 11 different mixtures.

**isotherm | isobar | flashpoint** If the subkey isotherm is included (default) a fixed temperature will be used. If the subkey isobar is included a fixed vapor pressure will be used. If the subkey flashpoint is included the flashpoint will be calculated.

**Links** COSMO-RS GUI tutorial: A composition line between solvents s1 and s2 [1]

## 4.8 Analysis

### 4.8.1 Sigma profile

The sigma profile of a mixture can be calculated with:

```
PROPERTY sigmaprofile
  {Nprofile nprofile}
  {SigmaMax sigmamax}
End
```

In case of a mixture the mole fraction of each compound in the mixture should be given with the subkey FRAC1 of the key COMPOUND for this compound.

The sigma profile pure compounds can be calculated with:

```
PROPERTY puresigmaprofile
{Nprofile nprofile}
{SigmaMax sigmamax}
End
```

**nprofile** Number of data points for which to calculate the sigma profile. default value 50.

**sigmamax** The sigma profile is calculated between -sigmamax and sigmamax. Default value 0.025.

The hydrogen bonding part (HB) of the sigma profile(s) will also be calculated. In case of a COSMO-SAC 2013-ADF calculation also the OH component of hydrogen bonding (HB-OH) is calculated, and the other type component of hydrogen bonding (HB-OT) is calculated.

**Links** COSMO-RS GUI tutorial: sigma profile [1]

## 4.8.2 Sigma potential

The sigma potential of a mixture can be calculated with:

```
PROPERTY sigmapotential
{Nprofile nprofile}
{SigmaMax sigmamax}
End
```

In case of a mixture the mole fraction of each compound in the mixture should be given with the subkey FRAC1 of the key COMPOUND for this compound.

The sigma profile pure compounds can be calculated with:

```
PROPERTY puresigmapotential
{Nprofile nprofile}
{SigmaMax sigmamax}
End
```

**nprofile** Number of data points for which to calculate the sigma potential. default value 50.

**sigmamax** The sigma potential is calculated between -sigmamax and sigmamax. Default value 0.025.

**Links** COSMO-RS GUI tutorial: sigma potential [1]



## SCRIPTING WITH COSMO-RS

## 5.1 ADFprep: construct an ADF COSMO results file

The module `adprep` is intended to facilitate scripting. More details on `adprep` can be found in the ADFprep section in the Scripting manual. For COSMO-RS the most relevant is the ADFCRS template. The template ADFCRS will perform a gas phase geometry optimization, and next a COSMO calculation at the gas phase optimized geometry.

In the next example the result of the ADF calculation is a file called `adfwater.coskf`, which is an ADF COSMO result file, that can be used as input for a COSMO-RS calculation, see also the *Example: COSMO-RS Tutorial 1* (page 37).

```
cat << eor > water.xyz
3

H      0.00000000      0.77121000      0.18071000
O      0.00000000     -0.00000000     -0.36142000
H      0.00000000     -0.77121000      0.18071000
eor

"$ADFBIN/adfprep" -t ADFCRS -m water.xyz -j adfwater >job
chmod +x job
./job
```

## 5.2 CRSprep: generate (multiple) COSMO-RS jobs

The module `crsprep` is intended to facilitate scripting: it makes it easier to construct proper jobs, from within a script. This module can be used, for example, to run the same type of COSMO-RS job on various compounds, or to change input settings. This module can also be used to put pure compound data on an ADF COSMO result file.

In `$ADFHOMe/examples/crs` one can find examples that follow the COSMO-RS GUI tutorials, which are also described in the section *Scripting Examples* (page 37). *Tutorial1* (page 37) uses `adprep` (page 33) to construct an ADF COSMO results file. *Tutorial2* (page 38), *Tutorial3* (page 39), *Tutorial4* (page 44), and *Tutorial5* (page 48) show different examples that use `crsprep` for COSMO-RS calculations.

The most convenient way to see the options of `crsprep` is to run the `crsprep` command without arguments. You will get output very much alike the following description, but probably more up-to-date.

```
% crsprep -h

CRSprepare (crsprep) saves pure compound data on an ADF COSMO result file
or generates a job script for COSMO-RS calculations,
with user specified changes to input options / method / system.
Required is at least 1 compound and -savecompound or -t template
```

Usage:

```

crsprep -savecompound -s compound.coskf
    [-nring nring] [-pvap pvap] [-tvap tvap] [-antoine "A B C"]
    [-meltingpoint meltingpoint] [-hfusion hfusion] [-cpfusion cpfusion]
    [-flashpoint flashpoint] [-density density] [-scalearea scalearea]
crsprep -t template
    [-s compound.(coskf|compoundlist)] [-c compound.(coskf|compoundlist)]
    [-nring nring] [-pvap pvap] [-tvap tvap] [-antoine "A B C"]
    [-meltingpoint meltingpoint] [-hfusion hfusion] [-cpfusion cpfusion]
    [-flashpoint flashpoint] [-density density] [-scalearea scalearea]
    [-frac1 frac1] [-frac2 frac2]
    [-densitysolvent densitysolvent] [-solphase solphase]
    [-volumequotient volumequotient] [-preset preset]
    [-method method] [-temperature temperature] [-pressure pressure]
    [-iso iso] [-n n] [-inputpurevap inputpurevap]
    [-inputpuredensity inputpuredensity]
    [-sigmax sigmax] [-massfraction] [-file filename] [-j jobname]

```

SAVE PURE COMPOUND DATA

```

-savecompound
    use to save pure compound data on an existing ADF COSMO result file

```

TEMPLATE

```

-t template
    use for COSMO-RS property calculation
    template should be one of:
        VAPORPRESSURE, PUREVAPORPRESSURE,
        BOILINGPOINT, PUREBOILINGPOINT, FLASHPOINT,
        LOGP, ACTIVITYCOEF, SOLUBILITY, PURESOLUBILITY,
        BINMIXCOEF, TERNARYMIX, COMPOSITIONLINE,
        SIGMAPROFILE, PURESIGMAPROFILE, SIGMAPOTENTIAL, PURESIGMAPOTENTIAL

```

COMPOUNDS

```

    at least 1 compound is required
-s file: the special compound(s) to be used, should be a .coskf file,
    or a .compoundlist file. The -s key has to be repeated for each file
-c file: additional compound(s) to be used, should be a .coskf file,
    or a .compoundlist file. The -c key has to be repeated for each file
    the order of the compounds is: first all compound defined with -s,
    then those with -c
LOGP, ACTIVITYCOEF, SOLUBILITY: use -s for the solvent and -c for the solutes
PURESOLUBILITY: use -s for the solute and -c for the solvents

```

PURE COMPOUND DATA

```

-nring: number of ring atoms
-pvap: pure compound vapor pressure (bar) at tvap
-tvap: at this temperature (Kelvin) pure compound has pressure pvap
-antoine: Antoine coefficients A, B, and C
-meltingpoint: melting point (Kelvin)
-hfusion: enthalpy of fusion (kcal/mol)
-cpfusion: heat capacity of fusion (kcal/(mol K))
-flashpoint: flash point (Kelvin)
-density: liquid density (kg/L)
-scalearea: COSMO surface area scale factor
    these keys can be repeated for each compound,
    first appearance of the key will be for compound 1, second for compound 2, etc.
    note the order of the compounds

```

```

SOLVENT
-frac1: define solvent
-frac2: define solvent 2 (LogP, composition line)
    the -frac1 and -frac2 key have to be repeated for
    each compound that should have a non-default value
    first appearance of the key will be for compound 1, second for compound 2, etc.
    note the order of the compounds
-densitiesolvent: density solvent (kg/L)
-solphase: pure compound phase solute in solubility calculation
-volumequotient: molar volume phase 1/molar volume phase 2 (LogP)
-preset: LogP preset 0, 2, 3, 4, 5
    0: user defined; 2: Octanol/Water; 3: Benzene/Water; 4: Ether/Water;
    5: Hexane/Water

METHOD, SYSTEM
-method: COSMO-RS, COSMOSAC2013
-temperature: temperature (Kelvin)
    the -temperature key can be used twice to give a range
-pressure: pressure (bar)
    the -pressure key can be used twice to give a range
-iso: isotherm, isobar, flashpoint
-n: number of steps
-inputpurevap: if 1 use input pure compound pvap and tvap or Antoine equation
-inputpuredensity: if 1 use input pure compound liquid density
-sigmax: maximum value sigma (sigma profile, sigma potential)
-massfraction: use mass fractions

INPUT FILE
-file: content of the file will be added at the end of the input for the
    COSMO-RS calculation. The -file key has to be repeated for each file

OUTPUT
-j: produce a fully runnable job (as the .job files from ADFjobs),
    using the specified jobname. The job script produces files like jobname.out,
    jobname.crskf etc. Several job scripts can simply be concatenated,
    the results will be stored in different files using the jobname parameter
    the default is a simple run script

EXAMPLES
crsprep -s benzene.coskf -nring 6 -savecompound
crsprep -t VAPORPRESSURE -temperature 273.15 -temperature 373.15 -s methanol.coskf

```

### 5.3 ADFreport: generate report

The module adfreport is intended to facilitate scripting. More details on adfreport can be found in the ADFreport section in the Scripting manual. It makes it very easy to get results calculated by COSMO-RS (or other programs in the ADF suite) in your own script. Compared to ADF2014 ADFreport has been extended to get easier results from COSMO-RS result files (.crskf files). It was already possible to report any proper KF variable from the .crskf file. Now a few predefined keys are added. See the \$ADFHOME/examples/crs directory for use of adfreport in COSMO-RS calculations. Depending on the kind of calculation one can use:

Command line option	Property
PROPERTY	General:Property
METHOD	Property:Method

NITEMS	Property:Number of Items
FRAC1	Property:Solvent: molar fraction
FRAC2	Property:Solvent 2: molar fraction
SOLVENT-FRACTION	Property:Solvent: solvent fraction
TEMPERATURE	Property:Temperature (in Kelvin)
PRESSURE	Property:Pressure (in bar)
GIBBS-ENERGY-MIXING	Property:Gibbs free energy of Mixing (in kcal/mol)
GIBBS-ENERGY-SOLVATION	Property:Gibbs free energy of Solvation (in kcal/mol)
GIBBS-ENERGY-SOLUTE	Property:Gibbs free energy solute (in kcal/mol)
EXCESS-G	Property:Excess Gibbs free energy (in kcal/mol)
EXCESS-H	Property:Excess Enthalpy (in kcal/mol)
ENTHALPY-VAPORIZATION	Property:Enthalpy of vaporization (in kcal/mol)
LOGP	Property:LogP
MOLAR-FRACTION	Property:Molar Fraction
ACTIVITY-COEFFICIENT	Property:Activity Coefficient
VAPOR-PRESSURE	Property:Vapor Pressure (in bar)
SOLUBILITY-X	Property:Solubility: molar fraction
SOLUBILITY-M	Property:Solubility: moles per liter (in mol/(L solution))
SOLUBILITY-G	Property:Solubility: gram per liter (in g/(L solution))
SOLUBILITY-MASS-FRACTION	Property:Solubility: mass fraction
HENRY	Property:Henry Constant (in mol/(L atm))
HENRY-NODIM	Property:Henry Constant dimensionless
MISCIBILITY-GAP	Property:Miscibility gap
MISCIBILITY-GAP-T	Property:Miscibility gap temperature (in Kelvin)
MISCIBILITY-GAP-P	Property:Miscibility gap pressure (in bar)
MISCIBILITY-GAP-X	Property:Miscibility gap molar fraction x1 x1'
MISCIBILITY-GAP-A	Property:Miscibility gap activities a1 a2
TIE-LINES-X	Property:Tie Lines molar fraction x1 x2 x3 x1' x2' x3'
TIE-LINES-A	Property:Tie Lines activities a1 a2 a3
CHEMICAL-POTENTIAL	Property:Chemical Potential
CHEMICAL-POTENTIAL-PURE	Property:Chemical Potential Pure Compounds Liquid
CHEMICAL-POTENTIAL-GAS	Property:Chemical Potential Pure Compounds Gas
SIGMA	Property:Sigma
SIGMA-PROFILE	Property:Sigma Profile
SIGMA-PROFILE-HB	Property:Sigma Profile Hydrogen Bonding part
SIGMA-PROFILE-TOTAL	Property:Total Sigma Profile
SIGMA-PROFILE-HB-TOTAL	Property:Total Sigma Profile Hydrogen Bonding part
SIGMA-POTENTIAL	Property:Sigma Potential
SIGMA-POTENTIAL-TOTAL	Property:Total Sigma Potential
NCOMP	Compounds:Number of Compounds
COMPOUNDS-FILENAME	Compounds:Filename
COMPOUNDS-NAME	Compounds:Name (from filename)
COMPOUNDS-MOLAR-MASS	Compounds:Molar Mass
Example	
"\$ADFBIN/adfreport" file.crskf ncomp	
"\$ADFBIN/adfreport" file.crskf ncomp -plain	

## 5.4 KF utilities for COSMO-RS

### 5.4.1 KF browser

With the GUI module kfbrowser one can browse through the raw data on KF files (like the .crskf COSMO-RS result files).



```
$ADFBIN/kfbrowser file.crskf
```

## 5.4.2 kf2cosmo and cosmo2kf

The two COSMO-RS command line utility programs *kf2cosmo* and *cosmo2kf* convert COSMO kf files from binary to ASCII and vice versa.

```
kf2cosmo file.coskf file.cosmo
```

*kf2cosmo* reads from the kf file *file.coskf* (should exist) the section ‘COSMO’ and writes to the ASCII file *file.cosmo* (should not exist). Instead of a *.coskf* file, the file can also be a TAPE21 file which is a result file from an ADF COSMO calculation.

```
cosmo2kf file.cosmo file.coskf
```

*cosmo2kf* reads from the ASCII file *file.cosmo* (should exist) and writes a section ‘COSMO’ to the kf file *file.coskf* (should not exist). Note that only a section ‘COSMO’ is written to the kf file, which means that this file can not be used like an ordinary TAPE21 (*.t21*) file.

```
cosmo2kf file.cos file.coskf
```

*cosmo2kf* can also read a MOPAC COSMO result file *file.cos* (should exist and should have the file extension *.cos*) and writes a section ‘COSMO’ to the kf file *file.coskf* (should not exist).

## 5.4.3 pkf, cpkf, dmpkf, udmpkf

```
pkf file.crskf
```

*pkf* prints a summary of the contents of a kf file

```
cpkf file.t21 file.coskf COSMO
```

With the ADF kf utility *cpkf* one can copy the section ‘COSMO’ from a *file.t21* (should exist) to a *file.coskf* (should not exist). The file *file.t21* should be a result of an ADF COSMO calculation. The file *file.coskf* is much smaller than *file.t21*. This file *file.coskf* can not be used like an ordinary *.t21* file, but it contains all necessary information such that it can be used as input for a COSMO-RS calculations.

With the ADF kf utilities *dmpkf* and *udmpkf* one can also convert COSMO kf files from binary to ASCII and vice versa. Note that the ASCII files in this case are not so called *.cosmo* files.

```
dmpkf file.coskf ascii_result
udmpkf ascii_result newfile.coskf
```

## 5.5 Scripting Examples

### 5.5.1 COSMO result files

*Sample directory:* *\$ADFHOME/examples/crs/Tutorial1*

This example tries to do the same as in the COSMO-RS GUI Tutorial: COSMO result files, using scripts.

In the first part of the example you will find how to use *adprep* to construct an ADF COSMO results file. The template *ADFCRS* will perform a gas phase geometry optimization (for water, in this case), and next a COSMO calculation at

the gas phase optimized geometry. The result file `adfwater.coskf`, which is an ADF COSMO result file, can be used as input for a COSMO-RS calculation.

```
cat << eor > water.xyz
3

H      0.00000000      0.77121000      0.18071000
O      0.00000000     -0.00000000     -0.36142000
H      0.00000000     -0.77121000      0.18071000
eor

"$ADFBIN/adfprep" -t ADFCRS -m water.xyz -j adfwater >job
chmod +x job
./job

"$ADFBIN/adfreport" adfwater.t21 geometry-a*
"$ADFBIN/adfreport" adfwater.coskf energies
```

In the second part of the example a MOPAC COSMO result file is constructed. The template MOPAC-GO will perform a COSMO geometry optimization. The result file `mopacwater.coskf`, which is a MOPAC COSMO result file, can be used as input for a COSMO-RS calculation.

```
"$ADFBIN/adfprep" -t MOPAC-GO -m water.xyz -g "mopac.solv COSMO-CRS" -j mopacwater >job
chmod +x job
./job

"$ADFBIN/adfreport" mopacwater.rkf geometry-a*
"$ADFBIN/adfreport" mopacwater.coskf energies
```

## 5.5.2 COSMO-RS parameters and analysis

*Sample directory:* `$ADFHOME/examples/crs/Tutorial2`

This example tries to part of the COSMO-RS GUI Tutorial: parameters and analysis, using scripts.

First some `.coskf` files are copied to the location where the scripts are running.

```
cp $ADFHOME/examples/crs/Tutorial2/benzene.coskf .
cp $ADFHOME/examples/crs/Tutorial2/ethanol.coskf .
cp $ADFHOME/examples/crs/Tutorial2/methanol.coskf .
cp $ADFHOME/examples/crs/Tutorial2/water.coskf .
```

### Set pure compound parameters

In the first part of the example you will find how to use `crsprep` to set pure compound parameters, in this case to set the number of ring atoms for the benzene molecule, which has 6 ring atoms. The file `benzene.coskf` is changed, such that it contains the value "6" for the number of ring compounds.

```
"$ADFBIN/crsprep" -c benzene.coskf -nring 6 -savecompound
```

### The sigma profile and the sigma potential

Next for convenience a file `tutorial2.compoundlist` is made that consists of 4 `coskf` files.

```
cat << eor > tutorial2.compoundlist
  benzene.coskf
  ethanol.coskf
  methanol.coskf
  water.coskf
eor
```

In the second part of the example sigma profiles are calculated for the four compounds (result file step6.crskf), and next the sigma potentials ( $\sigma$ -potential) of the four pure compounds (result file step7.crskf). With *adfreport* one can get the calculated sigma profile or sigma potential from the .crskf file on standard output.

```
"$ADFBIN/crsprep" -t PURESIGMAPROFILE -c tutorial2.compoundlist -j step6 > job
"$ADFBIN/crsprep" -t PURESIGMAPOTENTIAL -c tutorial2.compoundlist -j step7 >> job
chmod +x job
./job
echo "Results"
"$ADFBIN/adfreport" step6.crskf sigma
"$ADFBIN/adfreport" step6.crskf sigma-profile
"$ADFBIN/adfreport" step6.crskf sigma-profile-hb
"$ADFBIN/adfreport" step7.crskf sigma-potential
echo "Ready"
```

### 5.5.3 COSMO-RS properties

*Sample directory:* `$ADFHOME/examples/crs/Tutorial3`

This example tries to do the same as COSMO-RS GUI Tutorial: properties, using scripts.

This example starts with copying 4 coskf files to the current directory, and modifying the benzene.coskf file such that the number of ring atoms is 6, like in the previous example.

```
cp $ADFHOME/examples/crs/Tutorial2/benzene.coskf .
cp $ADFHOME/examples/crs/Tutorial2/ethanol.coskf .
cp $ADFHOME/examples/crs/Tutorial2/methanol.coskf .
cp $ADFHOME/examples/crs/Tutorial2/water.coskf .
"$ADFBIN/crsprep" -c benzene.coskf -nring 6 -savecompound
```

#### Step 2: Vapor pressure

In step 2 of the example the vapor pressure of methanol is calculated at the default temperature of 298.15 K (result file step2a.crskf), and next for a series of temperatures ranging from 273.15 K to 373.15 K in 10 steps (result file step2b.crskf).

```
"$ADFBIN/crsprep" -t PUREVAPORPRESSURE -j step2a \
  -c methanol.coskf > job
"$ADFBIN/crsprep" -t PUREVAPORPRESSURE -temperature 273.15 -temperature 373.15 \
  -j step2b \
  -c methanol.coskf >> job
./job
echo "Step 2a"
"$ADFBIN/adfreport" step2a.crskf temperature
"$ADFBIN/adfreport" step2a.crskf pressure
"$ADFBIN/adfreport" step2a.crskf enthalpy-vaporization
echo "Step 2b"
"$ADFBIN/adfreport" step2b.crskf temperature
```

```
"$ADFBIN/adfreport" step2b.crskf pressure
"$ADFBIN/adfreport" step2b.crskf enthalpy-vaporization
```

### Step 3: Boiling point

In step 3 of the example the boiling point of a mixture of methanol and ethanol is calculated, for a series of pressures ranging from 0.101325 to 1.01325 bar in 10 steps (result file step3.crskf). This mixture consist of 50% mole fraction methanol and 50% mole fraction ethanol.

```
"$ADFBIN/crsprep" -t BOILINGPOINT -pressure 0.101325 -pressure 1.01325 -j step3 \
-c methanol.coskf -frac1 0.5 \
-c ethanol.coskf -frac1 0.5 > job
./job
echo "Step 3"
"$ADFBIN/adfreport" step3.crskf temperature
"$ADFBIN/adfreport" step3.crskf pressure
```

### Step 4: Flash point

In step 4 of the example the flash point of a mixture of ethanol and water is calculated (result file step4.crskf). This mixture consist of 44.2% mass fraction methanol and 55.8% mass fraction ethanol. For a flash point calculation the pure compound flash points are needed as input, since COSMO-RS does not predict pure compound flash points. For pure ethanol a flash point of 286 K is saved in the file ethanol.coskf.

```
"$ADFBIN/crsprep" -c ethanol.coskf -flashpoint 286 -savecompound
"$ADFBIN/crsprep" -t FLASHPOINT -massfraction -j step4 \
-c ethanol.coskf -frac1 0.442 \
-c water.coskf -frac1 0.558 > job
./job
echo "Step 4 flash point"
"$ADFBIN/adfreport" step4.crskf temperature
```

### Step 5: Activity coefficients, Henry coefficients, Solvation free energies

In step 5 of the example the infinite diluted solutes benzene, methanol, and ethanol are calculated in the solvent water (result file step5.crskf). Activity coefficients, Henry coefficients and solvation free energies will be calculated. One one should include -s flag for water, since it is the solvent, and considered here to be a special compound.

```
"$ADFBIN/crsprep" -t ACTIVITYCOEF -j step5 \
-s water.coskf \
-c benzene.coskf -c ethanol.coskf -c methanol.coskf > job
./job
echo "Step 5 Activity coefficients, Henry's law constants, Solvation energy"
"$ADFBIN/adfreport" step5.crskf Activity-Coefficient
"$ADFBIN/adfreport" step5.crskf Henry
"$ADFBIN/adfreport" step5.crskf Gibbs-energy-solvation
```

### Step 6: Partition coefficients (log P)

In step 6 of the example the partition coefficients of infinitely diluted solutes in a mixture of two immiscible solvents are calculated. In step 6a the default Octanol/Water partition coefficients are calculated (default -preset 2) (result

file step6a.crskf). In step 6b a user defined (-preset 0) Benzene/Water partition coefficients are calculated (result file step6b.crskf). In this case one should include -s flag for benzene and water, since these are the two immiscible solvents, and considered here to be the special compounds. The order of the compounds benzene and water is important, because the molar volume of phase 1 (benzene) divided by the the molar volume of phase 2 (water) is given with the flag -volumequotient.

```
"$ADFBIN/crsprep" -t LOGP -j step6a \
-c benzene.coskf -c ethanol.coskf -c methanol.coskf > job
"$ADFBIN/crsprep" -t LOGP -preset 0 -volumequotient 4.93 -j step6b \
-s benzene.coskf -s water.coskf \
-c ethanol.coskf -c methanol.coskf >> job
./job
echo "Step 6a octanol/water"
"$ADFBIN/adfreport" step6a.crskf logp
echo "Step 6b benzene/water"
"$ADFBIN/adfreport" step6b.crskf logp
```

## Step 7: Solubility

In step 7 of the example the solubility of a compound is calculated. The solute can either be a liquid, solid, or gas. First some pure compound properties for benzene are set: the melting point, enthalpy of fusion, and the boiling point (file benzene.coskf).

```
"$ADFBIN/crsprep" -c benzene.coskf -meltingpoint 278.7 -hfusion 2.37 -savecompound
"$ADFBIN/crsprep" -c benzene.coskf -tvap 353.3 -pvap 1.01325 -savecompound
```

In step 7a the solubility of benzene in water is calculated for a range of temperatures ranging from 273.15 K to 373.15 K in 10 steps (result file step7a.crskf). If the template PURESOLUBILITY is used, the special compound is the solute, benzene in this case. Below 278.7 K, benzene is a solid. This will be taken into account, since the melting point and enthalpy of fusion are present on the file benzene.coskf. At higher temperatures benzene is assumed to be a liquid. Note that in this calculation above the normal boiling point of benzene the vapor pressure of benzene will be higher than 1.01325 bar.

```
"$ADFBIN/crsprep" -t PURESOLUBILITY -temperature 273.15 -temperature 373.15 -j step7a \
-s benzene.coskf \
-c water.coskf > job
```

In step 7b again the solubility of benzene in water is calculated for a (different) range of temperatures (result file step7b.crs) using the template SOLUBILITY. If the template SOLUBILITY is used, the special compound is the solvent, water in this case. For the density of the solvent water 1.0 kg/L is used. Below 278.7 K benzene is a solid. This will be taken into account, since the melting point and enthalpy of fusion are present on the file benzene.coskf. At higher temperatures benzene is assumed to be a liquid.

```
"$ADFBIN/crsprep" -t SOLUBILITY -temperature 273.15 -temperature 283.15 \
-densitysolvent 1.0 -j step7b \
-s water.coskf \
-c benzene.coskf >> job
```

In step 7c again the solubility of benzene in water is calculated for a range of temperatures above the boiling point of benzene (result file step7c.crs) using the template SOLUBILITY. If the template SOLUBILITY is used, the special compound is the solvent, water in this case. For the density of water 1.0 kg/L is used. For the vapor pressure of benzene 1.01325 bar is used.

```
"$ADFBIN/crsprep" -t SOLUBILITY -temperature 353.3 -temperature 373.15 \
-densitysolvent 1.0 -solphase Gas -pressure 1.01325 -j step7c \
-s water.coskf \
-c benzene.coskf >> job
```

The solubility of a gas in a solvent can also be calculated using Henry's law, which is valid for ideal dilute solutions. Henry coefficients can be calculated with the template ACTIVITYCOEF. In step 7d of the example the infinite diluted solutes benzene is calculated in the solvent water (result file step7d.crskf) at a temperature of 363.15 K. If the template ACTIVITYCOEF is used, the special compound is the solvent, water in this case. For the density of water 1.0 kg/L is used.

```
"$ADFBIN/crsprep" -t ACTIVITYCOEF -temperature 363.15 -densitysolvent 1.0 -j step7d \
-s water.coskf \
-c benzene.coskf >> job
```

Next the job is run which will produce the crskf files, and a report is made for all calculations in step 7.

```
./job
echo "Step 7a"
"$ADFBIN/adfreport" step7a.crskf solubility-x
echo "Step 7b"
"$ADFBIN/adfreport" step7b.crskf solubility-g
echo "Step 7c"
"$ADFBIN/adfreport" step7c.crskf solubility-m
echo "Step 7d"
"$ADFBIN/adfreport" step7d.crskf henry
```

### Step 8: Binary mixtures VLE/LLE

In step 8 phase diagrams of a mixture of two components are calculated with the template BINMIXCOEF. Exactly two compound should be given. In step 8a of the example a binary mixture of water and methanol is calculated at 298.14 K (result file step8a.crskf).

```
"$ADFBIN/crsprep" -t BINMIXCOEF -temperature 298.14 -j step8a \
-s water.coskf \
-s methanol.coskf > job
```

In step 8b of the example a binary mixture of water and ethanol is calculated at 322.45 K (result file step8b.crskf). Pure compound vapor pressures are given with -tvap (temperature in K) and -pvap (vapor pressure in bar). Preferably both -tvap and -pvap should be included for both compounds. If only one -tvap and one -pvap is given, it is assumed to be for the first compound. Note that these pure compound values are not saved to water.coskf or ethanol.coskf in this case.

```
"$ADFBIN/crsprep" -t BINMIXCOEF -temperature 322.45 -j step8b \
-s water.coskf -tvap 322.45 -pvap 0.123416 \
-s ethanol.coskf -tvap 322.45 -pvap 0.294896 >> job
```

In step 8c of the example a binary mixture of water and benzene is calculated at 323.15 K (result file step8c.crskf). Water and benzene do not mix very well. In this case a liquid-liquid equilibrium (LLE) will be calculated. The number of mixtures for which the binary mixture is calculated should be not too small, otherwise the properties of the 2 immiscible liquid phases will not be so accurate. In this case for the number of mixtures 100 is chosen. The actual number of mixtures is 5 more, thus 105 in this case.

```
"$ADFBIN/crsprep" -t BINMIXCOEF -temperature 323.15 -n 100 -j step8c \
-s water.coskf \
-s benzene.coskf >> job
```

In step 8d of the example a binary mixture of methanol and ethanol is calculated at a constant total vapor pressure (-iso isobar) of 1.01325 bar (result file step8d.crskf). Pure compound vapor pressures are given with -tvap (temperature in K) and -pvap (vapor pressure in bar). Preferably both -tvap and -pvap should be included for both compounds. If only one -tvap and one -pvap is given, it is assumed to be for the first compound. Note that these pure compound values are not saved to methanol.coskf or ethanol.coskf in this case.

```
"$ADFBIN/crsprep" -t BINMIXCOEF -iso isobar -pressure 1.01325 -j step8d \
-s methanol.coskf -tvap 338 -pvap 1.01325 \
-s ethanol.coskf -tvap 351 -pvap 1.01325 >> job
```

Next the job is run which will produce the crskf files, and a report is made for all calculations in step 8.

```
./job
echo "Step 8a"
"$ADFBIN/adfreport" step8a.crskf molar-fraction
"$ADFBIN/adfreport" step8a.crskf excess-g
"$ADFBIN/adfreport" step8a.crskf excess-h
echo "Step 8b"
"$ADFBIN/adfreport" step8b.crskf vapor-pressure
echo "Step 8c"
"$ADFBIN/adfreport" step8c.crskf miscibility-gap
"$ADFBIN/adfreport" step8c.crskf miscibility-gap-x
"$ADFBIN/adfreport" step8c.crskf miscibility-gap-a
echo "Step 8d"
"$ADFBIN/adfreport" step8d.crskf temperature
```

### Step 9: Ternary mixtures VLE/LLE

In step 9 phase diagrams of a mixture of three components are calculated with the template TERNARYMIX. Exactly three compound should be given. For convenience first some pure compound properties (normal boiling points) are saved to the .coskf files.

```
"$ADFBIN/crsprep" -c water.coskf -tvap 373.15 -pvap 1.01325 -savecompound
"$ADFBIN/crsprep" -c methanol.coskf -tvap 338 -pvap 1.01325 -savecompound
"$ADFBIN/crsprep" -c ethanol.coskf -tvap 351 -pvap 1.01325 -savecompound
"$ADFBIN/crsprep" -c benzene.coskf -tvap 353.3 -pvap 1.01325 -savecompound
```

In step 9a of the example a ternary mixture of methanol, ethanol, and benzene is calculated at 343.15 K (result file step9a.crskf). In step 9b of the example a ternary mixture of water, ethanol, and benzene is calculated at a constant total vapor pressure (-iso isobar) of 1.01325 bar (result file step9b.crskf). In step 9b a miscibility gap of the ternary mixture will be calculated. In this case, within the miscibility gap there are two immiscible phases of the liquid in equilibrium. The composition of the two phases, which are in equilibrium, can be found at the end points of the tie lines, that are calculated.

```
"$ADFBIN/crsprep" -t TERNARYMIX -temperature 343.15 -j step9a \
-s methanol.coskf -s ethanol.coskf -s benzene.coskf > job
"$ADFBIN/crsprep" -t TERNARYMIX -iso isobar -pressure 1.01325 -j step9b \
-s water.coskf -s ethanol.coskf -s benzene.coskf >> job

./job
echo "Step 9a"
"$ADFBIN/adfreport" step9a.crskf molar-fraction
"$ADFBIN/adfreport" step9a.crskf pressure
"$ADFBIN/adfreport" step9a.crskf miscibility-gap
echo "Step 9b"
"$ADFBIN/adfreport" step9b.crskf miscibility-gap
"$ADFBIN/adfreport" step9b.crskf tie-lines-x
"$ADFBIN/adfreport" step9b.crskf temperature
```

### Step 10: A composition line between solvents s1 and s2

In step 10 a phase diagram of a mixture of two solvents, which both are mixtures, is calculated with the template COMPOSITIONLINE. In this step one of the tie lines of the ternary mixture of water, ethanol, and benzene of step

9b will be investigated in more detail. Note that here the .coskf files are used in which the normal boiling points were saved to (in step 9). The mixture will be calculated for a list of molar (or mass) fractions of the solvents between zero and one, and the compositions of solvent 1 and solvent 2 are linearly interpolated. In this case solvent 1 consists of 0.3 molar fraction ethanol and 0.7 molar fraction benzene, and solvent 2 consists of 0.9 molar fraction water and 0.1 molar fraction ethanol. In step 10a of the example this mixture is calculated at a constant total vapor pressure (-iso isobar) of 1.01325 bar (result file step10a.crskf). In step 10b of the example this mixture is calculated at 341.05 K (result file step10b.crskf). Why this temperature was chosen can be found in step 10 of COSMO-RS GUI Tutorial: properties,

```
"$ADFBIN/crsprep" -t COMPOSITIONLINE -iso isobar -pressure 1.01325 -n 100 -j step10a \
-s water.coskf -frac1 0.0 -frac2 0.9 \
-s ethanol.coskf -frac1 0.3 -frac2 0.1 \
-s benzene.coskf -frac1 0.7 -frac2 0.0 > job
"$ADFBIN/crsprep" -t COMPOSITIONLINE -temperature 341.05 -n 100 -j step10b \
-s water.coskf -frac1 0.0 -frac2 0.9 \
-s ethanol.coskf -frac1 0.3 -frac2 0.1 \
-s benzene.coskf -frac1 0.7 -frac2 0.0 >> job
./job
echo "Step 10a"
$ADFBIN/adfreport step10a.crskf ncomp
$ADFBIN/adfreport step10a.crskf frac1
$ADFBIN/adfreport step10a.crskf frac2
$ADFBIN/adfreport step10a.crskf solvent-fraction
$ADFBIN/adfreport step10a.crskf molar-fraction
$ADFBIN/adfreport step10a.crskf activity-coefficient
echo "Step 10b"
$ADFBIN/adfreport step10b.crskf Gibbs-energy-mixing
```

## 5.5.4 The COSMO-RS compound database

*Sample directory: \$ADFHOME/examples/crs/Tutorial4*

This example tries to do the same as in the COSMO-RS GUI Tutorial: The COSMO-RS compound database, using scripts. In many of the next examples fewer compounds are included than in the COSMO-RS GUI Tutorial.

First some .coskf files are copied to the location where the scripts are running. These .coskf files are a sample of the full database.

```
cp $ADFHOME/examples/crs/Tutorial4/*.coskf .
```

### 4.2 Octanol-Water partition coefficients (log P<sub>ow</sub>)

```
"$ADFBIN/crsprep" -t LOGP -j t4.2 \
-c Methanol.coskf > job
./job
echo "4.2"
"$ADFBIN/adfreport" t4.2.crskf compounds-name
"$ADFBIN/adfreport" t4.2.crskf logp
```

### 4.3: Henry's law constants

```
"$ADFBIN/crsprep" -t ACTIVITYCOEF -temperature 293.15 -densitysolvent 0.998 -j t4.3a \
-s Water.coskf \
-c Acetone.coskf -c Benzene.coskf -c Ethanol.coskf \
-c Methanol.coskf > job
```



```

./job
echo "4.3a"
"$ADFBIN/adfreport" t4.3a.crskf compounds-name
"$ADFBIN/adfreport" t4.3a.crskf henry

"$ADFBIN/crsprep" -s Acetone.coskf -pvap 0.246 -tvap 293.15 -savecompound
"$ADFBIN/crsprep" -s Benzene.coskf -pvap 0.100 -tvap 293.15 -savecompound
"$ADFBIN/crsprep" -s Ethanol.coskf -pvap 0.059 -tvap 293.15 -savecompound
"$ADFBIN/crsprep" -s Methanol.coskf -pvap 0.129 -tvap 293.15 -savecompound
"$ADFBIN/crsprep" -s Water.coskf -pvap 0.02536 -tvap 293.15 -savecompound

"$ADFBIN/crsprep" -t ACTIVITYCOEF -temperature 293.15 -densitysolvent 0.998 -j t4.3b \
-s Water.coskf \
-c Benzene.coskf -c Ethanol.coskf -c Methanol.coskf > job

./job
echo "4.3b"
"$ADFBIN/adfreport" t4.3b.crskf henry

```

#### 4.4: Solubility of Vanillin in organic solvents

```

"$ADFBIN/crsprep" -s Vanillin.coskf -meltingpoint 355 -hfusion 5.35 -savecompound
"$ADFBIN/crsprep" -t PURESOLUBILITY -j t4.4 \
-s Vanillin.coskf \
-c Ethanol.coskf -c Methanol.coskf -c Water.coskf > job

./job
echo "4.4"
"$ADFBIN/adfreport" t4.4.crskf compounds-name
"$ADFBIN/adfreport" t4.4.crskf solubility-x
"$ADFBIN/adfreport" t4.4.crskf solubility-m

```

#### 4.5: Binary mixture of Methanol and Hexane

```

"$ADFBIN/crsprep" -s Methanol.coskf -pvap 0.845 -tvap 333.15 -savecompound
"$ADFBIN/crsprep" -s Hexane.coskf -pvap 0.77 -tvap 333.15 -savecompound
"$ADFBIN/crsprep" -t BINMIXCOEF -temperature 333.15 -n 100 -j t4.5a \
-s Methanol.coskf \
-s Hexane.coskf > job

./job
echo "4.5a"
"$ADFBIN/adfreport" t4.5a.crskf compounds-name
"$ADFBIN/adfreport" t4.5a.crskf molar-fraction
"$ADFBIN/adfreport" t4.5a.crskf pressure
"$ADFBIN/adfreport" t4.5a.crskf miscibility-gap
"$ADFBIN/adfreport" t4.5a.crskf miscibility-gap-x
"$ADFBIN/adfreport" t4.5a.crskf miscibility-gap-a

"$ADFBIN/crsprep" -s Methanol.coskf -pvap 1.01325 -tvap 337.8 -savecompound
"$ADFBIN/crsprep" -s Hexane.coskf -pvap 1.01325 -tvap 342 -savecompound
"$ADFBIN/crsprep" -t BINMIXCOEF -pressure 1.01325 -iso isobar -n 100 -j t4.5b \
-s Methanol.coskf \
-s Hexane.coskf > job

./job
echo "4.5b"
"$ADFBIN/adfreport" t4.5b.crskf molar-fraction
"$ADFBIN/adfreport" t4.5b.crskf temperature

```

```
"$ADFBIN/adfreport" t4.5b.crskf miscibility-gap
"$ADFBIN/adfreport" t4.5b.crskf miscibility-gap-x
"$ADFBIN/adfreport" t4.5b.crskf miscibility-gap-a
```

#### 4.6: Large infinite dilution activity coefficients in Water

```
"$ADFBIN/crsprep" -t ACTIVITYCOEF -temperature 298.15 -j t4.6 \
                  -s Water.coskf \
                  -c Benzene.coskf > job
./job
echo "4.6"
"$ADFBIN/adfreport" t4.6.crskf compounds-name
"$ADFBIN/adfreport" t4.6.crskf activity-coefficient
```

#### 4.7: Parametrization of ADF COSMO-RS: solvation energies, vapor pressures, partition coefficients

```
cat << eor > small.compoundlist
Hexane.coskf
Methanol.coskf
Ethanol.coskf
Acetone.coskf
Benzene.coskf
Water.coskf
eor

"$ADFBIN/crsprep" -t ACTIVITYCOEF -temperature 298.15 -densitysolvent 0.997 -j t4.7a \
                  -inputpurevap 0 \
                  -s Water.coskf \
                  -c small.compoundlist > job
./job
echo "4.7a"
"$ADFBIN/adfreport" t4.7a.crskf compounds-name
"$ADFBIN/adfreport" t4.7a.crskf gibbs-energy-solvation

"$ADFBIN/crsprep" -t PUREVAPORPRESSURE -temperature 298.15 -j t4.7b \
                  -c small.compoundlist -inputpurevap 0 > job
./job
echo "4.7b"
"$ADFBIN/adfreport" t4.7b.crskf compounds-name
"$ADFBIN/adfreport" t4.7b.crskf vapor-pressure

"$ADFBIN/crsprep" -t LOGP -j t4.7c -c small.compoundlist > job
./job
echo "4.7c Octanol/Water"
"$ADFBIN/adfreport" t4.7c.crskf compounds-name
"$ADFBIN/adfreport" t4.7c.crskf logp

"$ADFBIN/crsprep" -t LOGP -preset 5 -j t4.7d -c small.compoundlist > job
./job
echo "4.7d Hexane/Water"
"$ADFBIN/adfreport" t4.7d.crskf logp

"$ADFBIN/crsprep" -t LOGP -preset 3 -j t4.7e -c small.compoundlist > job
./job
echo "4.7e Benzene/Water"
```

```
"$ADFBIN/adfreport" t4.7e.crskf logp

"$ADFBIN/crsprep" -t LOGP -preset 4 -j t4.7f -c small.compoundlist > job
./job
echo "4.7f Ether/Water"
"$ADFBIN/adfreport" t4.7f.crskf logp
```

#### 4.8: COSMO-SAC 2013-ADF

```
"$ADFBIN/crsprep" -t PURESIGMAPROFILE -m COSMOSAC2013 -c Water.coskf \
-c Ethanol.coskf -j t4.8a > job
./job
echo "4.8a"
"$ADFBIN/adfreport" t4.8a.crskf sigma
"$ADFBIN/adfreport" t4.8a.crskf sigma-profile
"$ADFBIN/adfreport" t4.8a.crskf sigma-profile-hb

"$ADFBIN/crsprep" -s Methanol.coskf -density 0.7918 -savecompound
"$ADFBIN/crsprep" -s Ethanol.coskf -density 0.789 -savecompound
"$ADFBIN/crsprep" -s Acetone.coskf -density 0.791 -savecompound

"$ADFBIN/crsprep" -t LOGP -m COSMOSAC2013 -j t4.8b -c Methanol.coskf \
-c Ethanol.coskf -c Acetone.coskf > job
./job
echo "4.8b Octanol/Water"
"$ADFBIN/adfreport" t4.8b.crskf compounds-name
"$ADFBIN/adfreport" t4.8b.crskf logp

"$ADFBIN/crsprep" -t LOGP -m COSMOSAC2013 -preset 5 -j t4.8c -c Methanol.coskf \
-c Ethanol.coskf -c Acetone.coskf > job
./job
echo "4.8c Hexane/Water"
"$ADFBIN/adfreport" t4.8c.crskf logp

"$ADFBIN/crsprep" -t LOGP -m COSMOSAC2013 -preset 3 -j t4.8d -c Methanol.coskf \
-c Ethanol.coskf -c Acetone.coskf > job
./job
echo "4.8d Benzene/Water"
"$ADFBIN/adfreport" t4.8d.crskf logp

"$ADFBIN/crsprep" -t LOGP -m COSMOSAC2013 -preset 4 -j t4.8e -c Methanol.coskf \
-c Ethanol.coskf -c Acetone.coskf > job
./job
echo "4.8e Ether/Water"
"$ADFBIN/adfreport" t4.8e.crskf logp

"$ADFBIN/crsprep" -s Acetone.coskf -density 0.791 \
-pvap 3.7 -tvap 373.15 -savecompound
"$ADFBIN/crsprep" -s Water.coskf -density 0.997 \
-pvap 1.01325 -tvap 373.15 -savecompound

"$ADFBIN/crsprep" -t BINMIXCOEF -m COSMOSAC2013 -temperature 373.15 -n 20 -j t4.8f \
-s Acetone.coskf \
-s Water.coskf > job
./job
echo "4.8f"
"$ADFBIN/adfreport" t4.8f.crskf molar-fraction
```

```
"$ADFBIN/adfreport" t4.8f.crskf vapor-pressure  
"$ADFBIN/adfreport" t4.8f.crskf pressure
```

### 5.5.5 pKa values

*Sample directory: \$ADFHOME/examples/crs/Tutorial5*

This example tries to do the same as in the COSMO-RS GUI Tutorial: pKa values, First some .coskf files are copied to the location where the scripts are running, next the jobs are prepared and the reports are made. Check the COSMO-RS GUI Tutorial: pKa values what to do with the results.

```
cp $ADFHOME/examples/crs/Tutorial5/*.coskf .  
cp $ADFHOME/examples/crs/Tutorial5/*compoundlist .  
  
echo "Acids"  
"$ADFBIN/crsprep" -t ACTIVITYCOEF -j t5.1a \  
                  -c tutorial5.1_acid.compoundlist > job  
./job  
"$ADFBIN/adfreport" t5.1a.crskf compounds-name  
"$ADFBIN/adfreport" t5.1a.crskf Activity-Coefficient  
"$ADFBIN/adfreport" t5.1a.crskf Gibbs-energy-solvation  
"$ADFBIN/adfreport" t5.1a.crskf Gibbs-energy-solute  
  
echo "Bases"  
"$ADFBIN/crsprep" -t ACTIVITYCOEF -j t5.1b \  
                  -c tutorial5.1_base.compoundlist > job  
./job  
"$ADFBIN/adfreport" t5.1b.crskf compounds-name  
"$ADFBIN/adfreport" t5.1b.crskf Activity-Coefficient  
"$ADFBIN/adfreport" t5.1b.crskf Gibbs-energy-solvation  
"$ADFBIN/adfreport" t5.1b.crskf Gibbs-energy-solute  
  
echo "Ready"
```

## REQUIRED CITATIONS

When you publish results in the scientific literature that were obtained with programs of the ADF package, you are required to include references to the program package with the appropriate release number, and a few key publications.

### 6.1 General References

For calculations with the COSMO-RS program, version 2016:

1. C.C. Pye, T. Ziegler, E. van Lenthe, J.N. Louwen, *An implementation of the conductor-like screening model of solvation within the Amsterdam density functional package. Part II. COSMO for real solvents*, *Can. J. Chem.* **87**, 790 (2009) (<http://dx.doi.org/10.1139/V09-008>)
2. ADF2016 COSMO-RS, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, <http://www.scm.com> Optionally, you may add the following list of authors and contributors: J.N. Louwen, C.C. Pye, E. van Lenthe, E.S. McGarrity, R. Xiong, S.I. Sandler, R.I. Burnett

If you use COSMO-SAC 2013-ADF you must also add

3. R. Xiong, S.I. Sandler, R.I. Burnett, *An improvement to COSMO-SAC for predicting thermodynamic properties*, *Ind. Eng. Chem. Res.* **53**, 8265 (2014) (<http://dx.doi.org/10.1021/ie404410v>)

### 6.2 External programs and Libraries

Click here for the list of programs and/or libraries used in the ADF package. On some platforms optimized libraries have been used and/or vendor specific MPI implementations.



## REFERENCES

1. A. Klamt, *Conductor-like Screening Model for Real Solvents: A New Approach to the Quantitative Calculation of Solvation Phenomena*. *J. Phys. Chem.* 99, 2224 (1995) (<http://dx.doi.org/10.1021/j100007a062>)
2. A. Klamt, V. Jonas, T. Bürger and J.C. Lohrenz, *Refinement and Parametrization of COSMO-RS*. *J. Phys. Chem. A* 102, 5074 (1998) (<http://dx.doi.org/10.1021/jp980017s>)
3. A. Klamt, *COSMO-RS From Quantum Chemistry to Fluid Phase Thermodynamics and Drug Design*, Elsevier. Amsterdam (2005), ISBN 0-444-51994-7.
4. C.C. Pye, T. Ziegler, E. van Lenthe, J.N. Louwen, *An implementation of the conductor-like screening model of solvation within the Amsterdam density functional package. Part II. COSMO for real solvents*. *Can. J. Chem.* 87, 790 (2009) (<http://dx.doi.org/10.1139/V09-008>)
5. B. Delley, *The conductor-like screening model for polymers and surfaces*. *Molecular Simulation* 32, 117 (2006) (<http://dx.doi.org/10.1080/08927020600589684>)
6. S. Wang, S.I. Sandler, C.C. Chen, *Refinement of COSMO-SAC and the Applications*, *Ind. Eng. Chem. Res.* 46, 7275 (2007) (<http://dx.doi.org/10.1021/ie070465z>)
7. C.M. Hsieh, S.I. Sandler, S.T. Lin, *Improvements of COSMO-SAC for vapor-liquid and liquid-liquid equilibrium predictions*, *Fluid Phase Equilib.* 297, 90 (2010) (<http://dx.doi.org/10.1016/j.fluid.2010.06.011>)
8. S.T. Lin and S.I. Sandler, *A Priori Phase Equilibrium Prediction from a Segment Contribution Solvation Model*, *Ind. Eng. Chem. Res.* 41, 899 (2002) (<http://dx.doi.org/10.1021/ie001047w>)
9. R. Xiong, S.I. Sandler, R.I. Burnett, *An improvement to COSMO-SAC for predicting thermodynamic properties*, *Ind. Eng. Chem. Res.* 53, 8265 (2014) (<http://dx.doi.org/10.1021/ie404410v>)





## KEYWORDS

- *COMPOUND* (page 24)
- *COSMOSAC* (page 21)
- *COSMOSAC2013* (page 21)
- *CRSPARAMETERS* (page 19)
- *DISPERSION* (page 20)
- *EPSILON* (page 22)
- *MASSFRACTION* (page 26)
- *PRESSURE* (page 25)
- *PROPERTY activitycoef* (page 28)
- *PROPERTY binmixcoef* (page 29)
- *PROPERTY boilingpoint* (page 26)
- *PROPERTY compositionline* (page 30)
- *PROPERTY flashpoint* (page 27)
- *PROPERTY logp* (page 27)
- *PROPERTY pureboilingpoint* (page 26)
- *PROPERTY puresigmapotential* (page 31)
- *PROPERTY puresigmaprofile* (page 31)
- *PROPERTY puresolubility* (page 28)
- *PROPERTY purevaporpressure* (page 26)
- *PROPERTY sigmapotential* (page 31)
- *PROPERTY sigmaprofile* (page 30)
- *PROPERTY solubility* (page 28)
- *PROPERTY ternarymix* (page 29)
- *PROPERTY vaporpressure* (page 26)
- *TECHNICAL* (page 23)
- *TEMPERATURE* (page 25)



## Symbols

.cos file, 17  
 .coskf file, 11  
 .cosmo file, 9  
 .t21 file, 11

## A

activity coefficients, 28  
 ADF COSMO calculation, 11  
 ADF COSMO settings, 11  
 ADFCRS-2010, 15  
 ADFCRS-IL-2014, 16  
 adfprep module, 33  
 adfreport module, 35

## B

binary mixture, 29  
 boiling point, 26

## C

calculation of properties, 6  
 cavity construction:, 13  
 combinatorial term, 5  
 composition line, 30  
 compounds, 24  
 COSKF file, 11  
 COSMO accuracy:, 13  
 COSMO cavity construction:, 13  
 COSMO file, 11  
 COSMO result file, 9  
 COSMO-RS parameters, 19  
 COSMO-RS program, 17  
 COSMO-RS theory, 3  
 COSMO-SAC, 6  
 COSMO-SAC 2013-ADF, 6  
 COSMO-SAC 2013-ADF parameters, 21  
 COSMO-SAC parameters, 21  
 COSMO-SAC theory, 6  
 cosmo2kf, 36  
 crsprep module, 33

## E

element specific parameters, 20

examples, 37  
 excess energies, 29  
 execution of COSMO-RS, 19

## F

fast approximation, 5  
 flash point, 27

## H

Henry's law constants, 28  
 hydrogen bond interaction, 6

## I

infinite dilute, 28

## K

kf2cosmo, 36

## L

LLE binary mixture, 29  
 LLE diagram, 29  
 LLE ternary mixture, 29  
 log P, 27

## M

mass fractions, 26  
 molar fractions, 26  
 MOPAC COSMO file, 16  
 MOPAC COSMO settings, 16

## O

Octanol/Water partition coefficients, 27

## P

partition coefficients, 27  
 pKa values, 28

## S

scripting examples, 37  
 sigma potential:, 31  
 sigma profile, 30

solubility, 28  
solvation energies, 28  
solvent boiling point, 26  
solvent flash point, 27  
solvent vapor pressure, 26

## T

ternary mixture, 29  
theory COSMO-RS, 3  
theory COSMO-SAC, 6  
Tutorial 1, 37  
Tutorial 2, 38  
Tutorial 3, 39  
Tutorial 4, 44  
Tutorial 5, 48

## V

vapor pressure, 26  
VLE binary mixture, 29  
VLE diagram, 29  
VLE ternary mixture, 29