Virginia Tech

Using the VT-2005 database

A step-by-step tutorial on predicting liquid-phase activity coefficients using the VT-2005 sigma profiles and the COSMO-SAC-VT-2005 program

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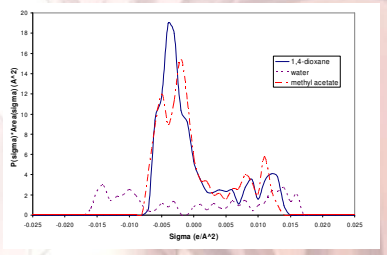
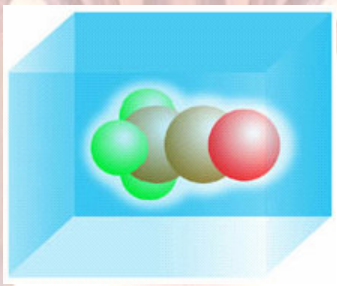
This presentation shows how to use VT-2005 sigma profiles with the COSMO-SAC-VT-2005 program to predict activity coefficients



1. Overview of sigma profiles



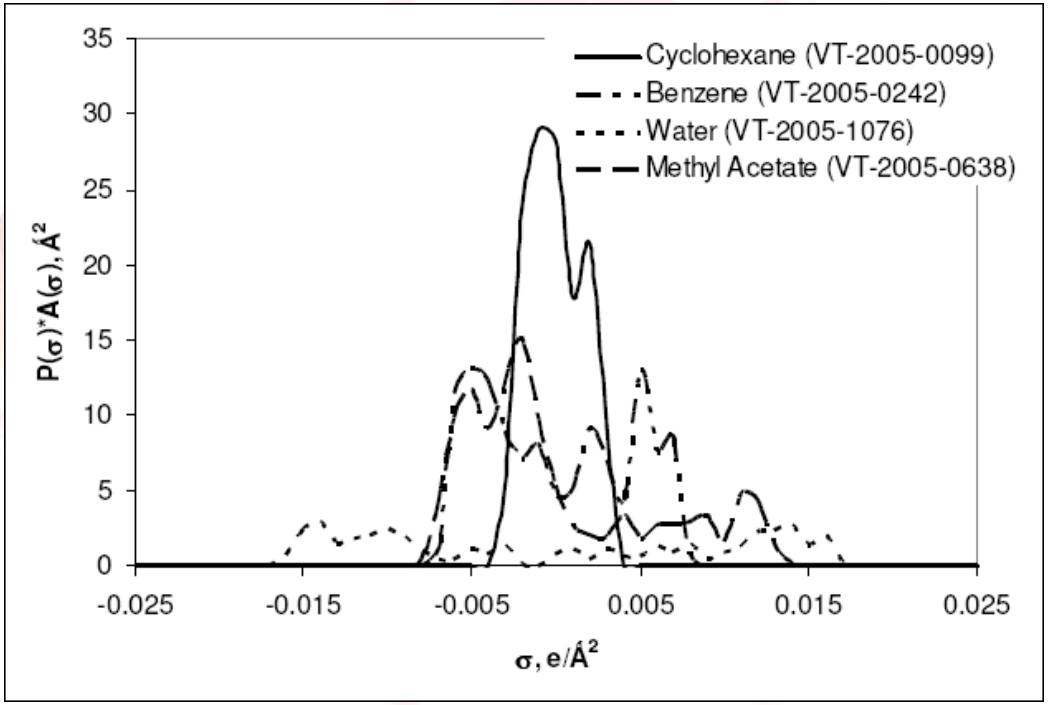
2. Outline of the COSMO-SAC model

COSMO-SAC-VT-2005.exe

3. Using the COSMO-SAC-VT-2005 program

The sigma profile depicts the surface charge distribution over the entire molecule.

- Graphically: Area vs. charge/Area
- Unique to each molecule
- Profiles are stored in a database
- Sigma profiles are not specific to a COSMO extension

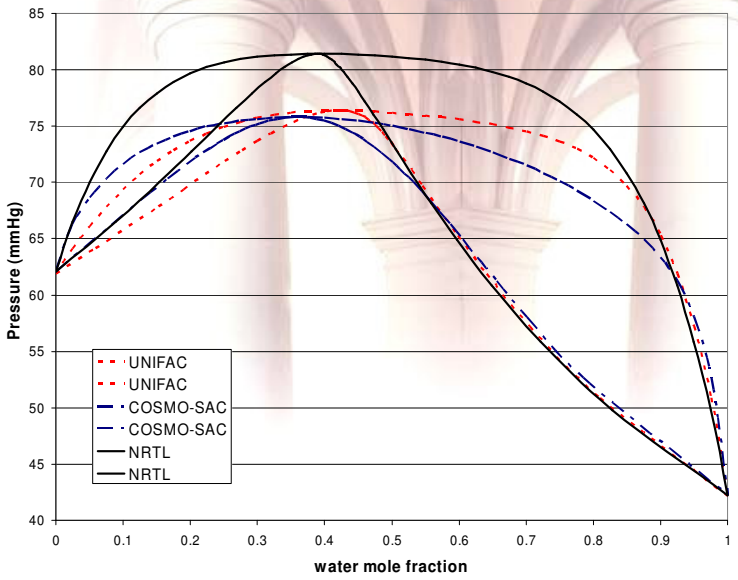


Sigma profile [*P(σ)*] = the probability a specific surface segment will have a specific charge density.

COSMO models use sigma profiles to predict physical properties.

- Solubility (SLE)
- Vapor-Liquid (VLE)
- Partition coefficients (K_{OW})
- pKa

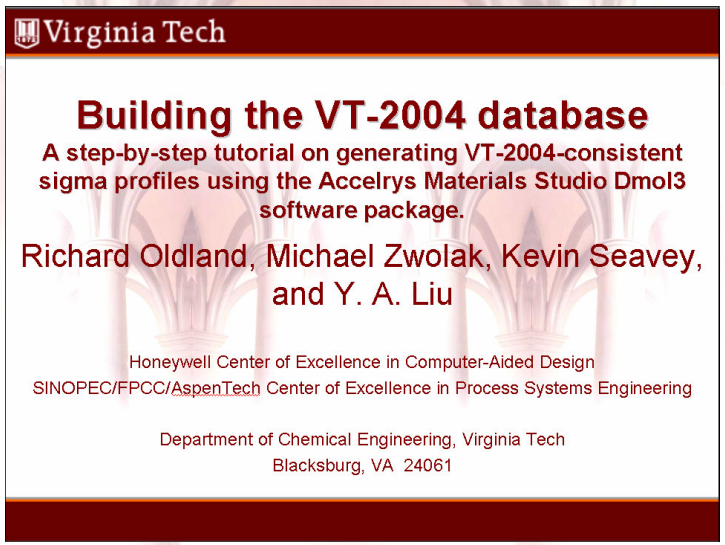
$P(\sigma)$ ⇒ **COSMO-SAC or COSMO-RS**



We develop the VT-2005 sigma-profile database containing over 1200 molecules.

Chemical components including alcohols, alkanes, fluorocarbons, ketones, aldehydes, solvents, etc.

The molecules contain the following elements: C, O, H, N, I, Cl, F, Br, P, F



We create sigma profiles in a format that is usable with COSMO-SAC-VT-2005 program.

Sigma values (e/Å^2) [x-axis]

P(σ) values (Å^2) [y-axis]

propane SIGMA-PROFILE.TXT - Notepad

File Edit Format Help

-2.500000000000000E-002	0.000000000000000E+000
-2.400000000000000E-002	0.000000000000000E+000
-2.300000000000000E-002	0.000000000000000E+000
-2.200000000000000E-002	0.000000000000000E+000
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-2.000000000000000E-002	0.000000000000000E+000
-1.900000000000000E-002	0.000000000000000E+000
-1.800000000000000E-002	0.000000000000000E+000
-1.700000000000000E-002	0.000000000000000E+000
-1.600000000000000E-002	0.000000000000000E+000
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-6.999999999999999E-003	0.000000000000000E+000
-6.000000000000002E-003	0.000000000000000E+000
-5.000000000000001E-003	0.000000000000000E+000
-4.000000000000000E-003	0.557737150791084
-3.000000000000003E-003	9.51638983386880
-2.000000000000002E-003	14.1093198091048
-1.000000000000001E-003	19.2525282558516
0.000000000000000E+000	13.0440922291662
1.000000000000001E-003	15.9768151546843
1.999999999999998E-003	16.7911938838134
2.999999999999999E-003	8.02136074779866
4.000000000000000E-003	0.356412934921149
4.999999999999998E-003	0.000000000000000E+000
5.999999999999998E-003	0.000000000000000E+000
6.999999999999999E-003	0.000000000000000E+000
8.000000000000000E-003	0.000000000000000E+000
9.000000000000001E-003	0.000000000000000E+000
1.000000000000000E-002	0.000000000000000E+000
1.100000000000000E-002	0.000000000000000E+000
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2.200000000000000E-002	0.000000000000000E+000
2.300000000000000E-002	0.000000000000000E+000
2.400000000000000E-002	0.000000000000000E+000

The output file 'Chemical' Sigma-profile.txt is located in the 'C:\Profiles\' directory by default.Å

We can either use this file directly in the COSMO-SAC program or we can plot it in MS Excel.

Lin and Sandler (2002) develop the continuum-solvation model COSMO-SAC

Model traits

- Extension to COSMO
- Liquid phase interactions
- Thermodynamically consistent

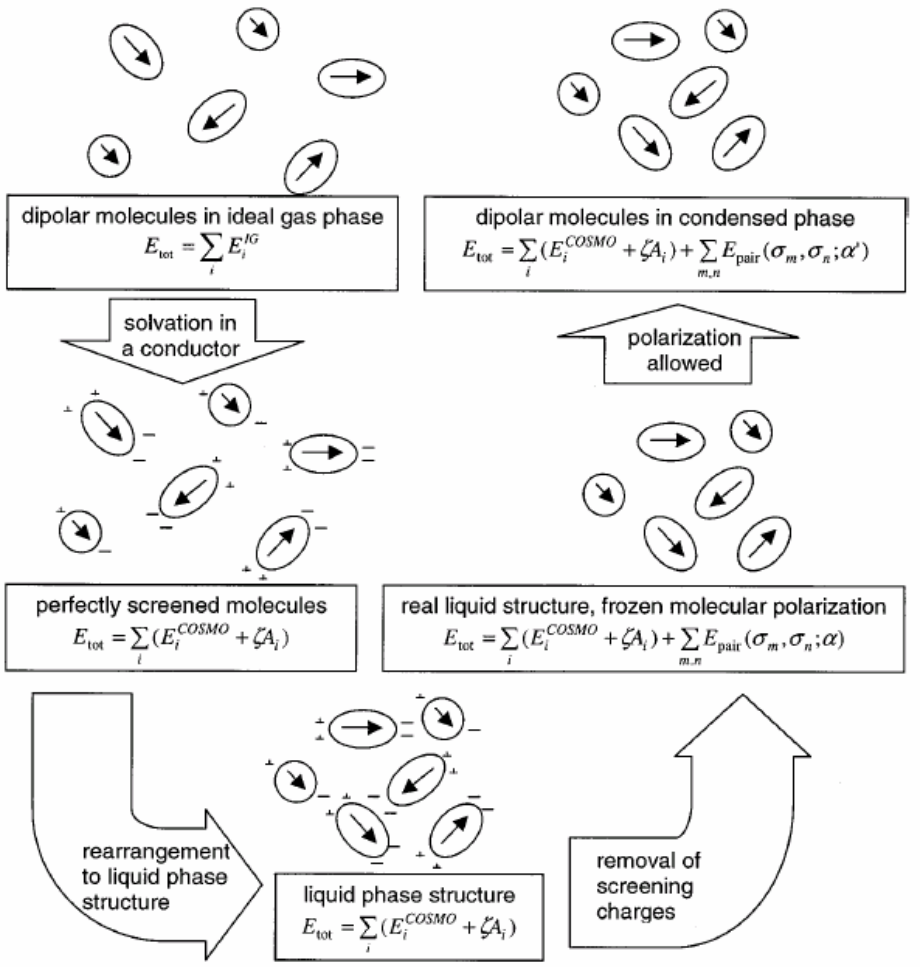
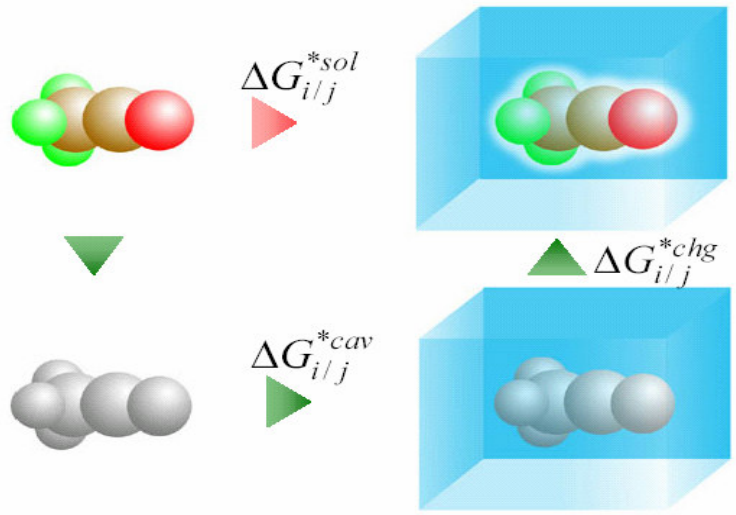


Figure from:
Lin and Sandler (2002a)

We begin with the definition of the solvation free energy (ΔG_{sol})



$\Delta G_{i/j}^{*sol}$: solvation free energy
$\Delta G_{i/j}^{*cav}$: cavity formation free energy
$\Delta G_{i/j}^{*chg}$: charging free energy
i/j : solute *i* in solvent *j*
c : total molar concentration

We break the real solvation process into two "ideal" steps:

1. Cavity formation
2. Charge restoration

Previous models for the activity coefficient use the free energy of solvation.

$$\ln \gamma_{i/S} = \frac{\Delta G_{i/S}^{*sol} - \Delta G_{i/i}^{*sol}}{RT} + \ln \frac{c_S}{c_i}$$

In terms of the solvation free energy (Ben-Naim (1987))

$$\ln \gamma_{i/S} = \frac{\Delta G_{i/S}^{*res} - \Delta G_{i/i}^{*res}}{RT} + \ln \gamma_{i/S}^{SG}$$

In terms of the charge restoring free energy. (Lin and Sandler (2002a))

The authors approximate the solvation process with the charge restoration free energy. We calculate this quantity with sigma profiles and activity coefficients for each surface segment.

The COSMO-SAC model predicts the activity coefficient using the sigma profile.

$$\ln \gamma_{i/S} = \frac{\Delta G_{i/S}^{*res} - \Delta G_{i/i}^{*res}}{RT} + \ln \gamma_{i/S}^{SG}$$

Starting with the charge restoring free energy

$$\frac{\Delta G_{i/S}^{*res}}{RT} = \sum_{\sigma_m} \left[n_i(\sigma_m) \frac{\Delta G_{\sigma_m/S}^{*res}}{RT} \right] = n_i \sum_{\sigma_m} p_i(\sigma_m) \ln \Gamma_S(\sigma_m)$$

$$\frac{\Delta G_{i/i}^{*res}}{RT} = \sum_{\sigma_m} \left[n_i(\sigma_m) \frac{\Delta G_{\sigma_m/i}^{*res}}{RT} \right] = n_i \sum_{\sigma_m} p_i(\sigma_m) \ln \Gamma_i(\sigma_m)$$

In terms of the sigma profile and the segment activity coefficient

$$\ln \gamma_{i/S} = n_i \sum_{\sigma_m} p_i(\sigma_m) \left[\ln \Gamma_S(\sigma_m) - \ln \Gamma_i(\sigma_m) \right] + \ln \gamma_{i/S}^{SG}$$

★ **Rigorous derivation included in Lin and Sandler 2002**

We provide the COSMO-SAC-VT-2005 program to predict activity coefficients

The COSMO-SAC-VT-2005 program is:

- FORTRAN90 based
- Open literature
- Quick to run
- Binary mixtures only
- Easily upgradeable for ternary and quaternary mixtures

Calculates liquid-phase activity coefficients for mole fractions ranging from 0.005-0.995 in steps of 0.01

Locate the pure component sigma profiles

This program is compatible with sigma profiles in a format similar to the VT-2005 sigma profiles.

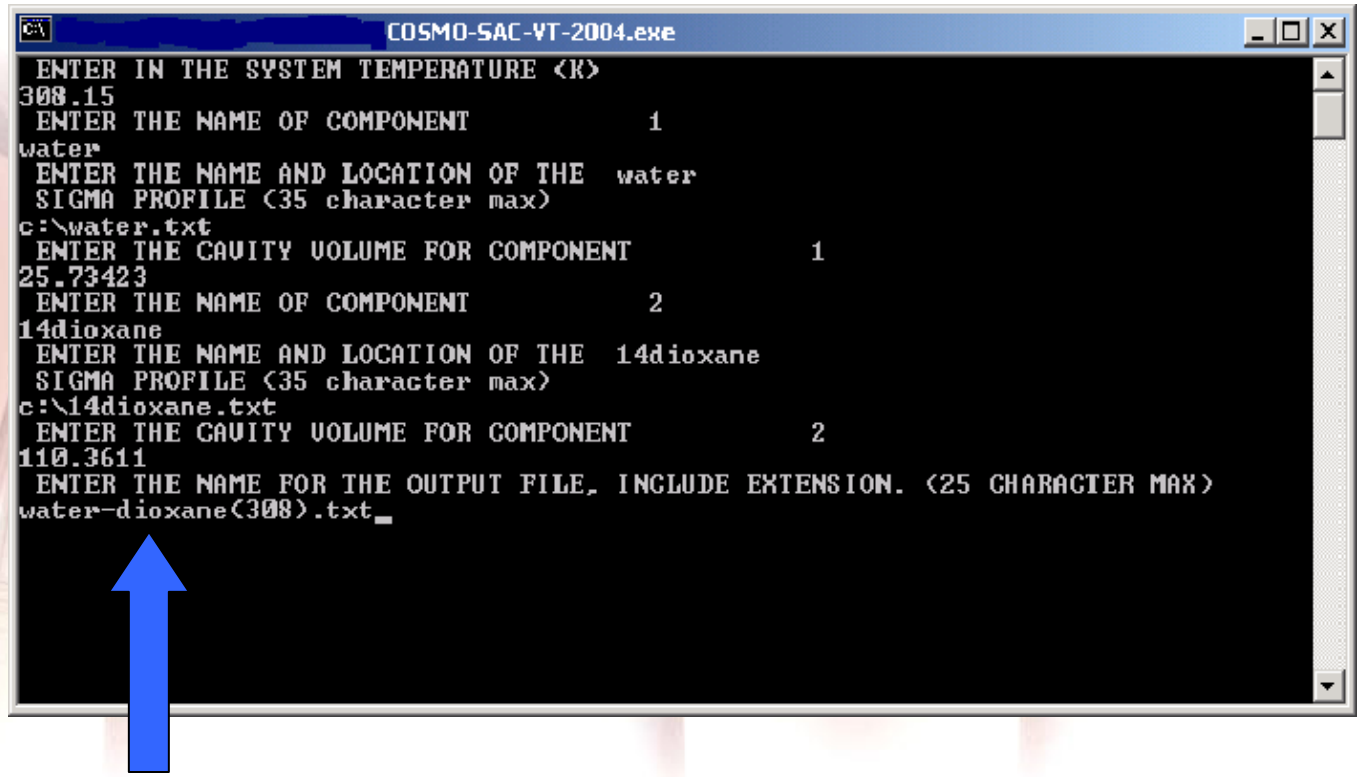
COSMO-SAC-VT-2005.exe requires the profile name AND location.

We store our sigma profiles in a central directory "C:\Profiles" to make them easy to locate. Create the directories "C:\Profiles" and "C:\Profiles\Gammas" at this time.

Run "COSMO-SAC-VT-2005.exe" and follow the MS-DOS prompts

Required inputs:

- System temperature
- Species names
- VT-2005 sigma profiles
- Cavity volumes
- Output file name



Creates the output file in the directory "C:\Profiles\Gammas" by default.

COSMO-SAC-VT-2005.exe creates an output text file

The output file is in the format:
Mole fraction component 1, γ_1 , γ_2 , Ln(γ_1), Ln(γ_2)

We can use the output to compare activity coefficient predictions or to predict physical properties

water-dioxane(308).txt - Notepad

File Edit Format Help

SYSTEMP 308.1500 KELVIN

MOLE FRAC X1	GAMMA1 water	GAMMA2 14dioxane	LNGAMMA1 water	LNGAMMA2 14dioxane
4.9999999E-03	6.823039	1.000270	1.920305	2.7009178E-04
1.5000000E-02	5.818343	1.001831	1.761015	1.8290234E-03
2.4999999E-02	5.177711	1.004194	1.644363	4.1850135E-03
3.4999996E-02	4.714868	1.007092	1.550721	7.0664957E-03
4.4999994E-02	4.357460	1.010394	1.471889	1.0340567E-02
5.4999992E-02	4.069511	1.014029	1.403523	1.3931060E-02
6.4999990E-02	3.830516	1.017948	1.343000	1.7788399E-02
7.4999988E-02	3.627705	1.022119	1.288600	2.1878084E-02
8.4999986E-02	3.452610	1.026521	1.239130	2.6175151E-02
9.4999984E-02	3.299349	1.031139	1.193725	3.0663570E-02
0.1050000	3.163669	1.035959	1.151732	3.5327226E-02
0.1150000	3.042414	1.040972	1.112651	4.0154886E-02
0.1250000	2.933175	1.046173	1.076086	4.5138836E-02
0.1350000	2.834075	1.051558	1.041716	5.0272778E-02
0.1450000	2.743635	1.057122	1.009284	5.5550113E-02
0.1550000	2.660658	1.062866	0.9785736	6.0968783E-02
0.1650000	2.584173	1.068786	0.9494057	6.6523783E-02
0.1750000	2.513373	1.074883	0.9216256	7.2212249E-02
0.1850000	2.447593	1.081157	0.8951051	7.8031957E-02
0.1950000	2.386264	1.087611	0.8697291	8.3983183E-02
0.2050000	2.328917	1.094244	0.8454031	9.0063281E-02
0.2150000	2.275136	1.101060	0.8220396	9.6273601E-02
0.2250000	2.224571	1.108061	0.7995640	0.1026120
0.2350000	2.176920	1.115250	0.7779109	0.1090789
0.2450000	2.131915	1.122631	0.7570206	0.1156752
0.2550000	2.089323	1.130209	0.7368400	0.1224027
0.2650000	2.048940	1.137984	0.7173225	0.1292584
0.2750000	2.010586	1.145966	0.6984261	0.1362482
0.2850000	1.974097	1.154155	0.6801109	0.1433689
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0.3050000	1.906158	1.171190	0.6450895	0.1580199
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0.3250000	1.844145	1.189135	0.6120158	0.1732259
0.3349999	1.815105	1.198466	0.5961432	0.1810427
0.3449999	1.787262	1.208049	0.5806846	0.1890063
0.3549999	1.760535	1.217889	0.5656180	0.1971191
0.3649999	1.734854	1.227997	0.5509235	0.2053840
0.3749999	1.710155	1.238382	0.5365842	0.2138053
0.3849999	1.686378	1.249054	0.5225832	0.2223861
0.3949999	1.663470	1.260024	0.5089056	0.2311311
0.4049999	1.641377	1.271305	0.4955357	0.2400439
0.4149999	1.620058	1.282907	0.4824621	0.2491286
0.4249999	1.599465	1.294847	0.4696692	0.2583928
0.4349999	1.579563	1.307136	0.4571481	0.2678382
0.4449998	1.560313	1.319789	0.4448865	0.2774721
0.4549998	1.541680	1.332824	0.4328729	0.2873003
0.4649998	1.523633	1.346261	0.4210974	0.2973310
0.4749998	1.506143	1.360116	0.4095520	0.3075698
0.4849998	1.489181	1.374410	0.3982263	0.3180242
0.4949998	1.472722	1.389165	0.3871122	0.3287026
0.5049998	1.456740	1.404405	0.3762011	0.3396137

Congratulations!

You have successfully used the COSMO-SAC model, COSMO-SAC-VT-2005.exe, to predict liquid-phase activity coefficients for a binary mixture.

Acknowledgements

Sinopec Corp.
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A technology leader in aerospace and defense

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Honeywell

Honeywell Specialty Materials

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We used the following articles in developing this procedure.

Klamt, Andreas, G. Shüürmann, "COSMO-A New Approach to Dielectric Screening in Solvents with Explicit Expressions for the Screening Energy and Its Gradient", *J. Chem. Soc. Perkin Trans.*, **2**, 799, (1993).

Klamt, Andreas, "Conductor-like Screening Model for Real Solvents: A New Approach to the Quantitative Calculation of Solvation Phenomena" , *J. Phys. Chem* , **99**, 2224 (1995).

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Lin, Shiang-Tai, "Quantum Mechanical Approaches to the Prediction of Phase Equilibria: Solvation Thermodynamics and Group Contribution Methods", PhD. Dissertation, University of Delaware, Newark, DE, 2000

Lin, Shiang-Tai and Stanley I. Sandler, "A Priori Phase Equilibrium Prediction from a Segment Contribution Solvation Model", *Ind. Eng. Chem. Res,* **41**, 899(2002a).

Lin, Shiang-Tai and Stanley I. Sandler, "Reply to Comments on "A Priori Phase Equilibrium Prediction from a Segment Contribution Solvation Model" *Ind. Eng. Chem. Res.,* **41**, 2332 (2002b).