

Current status of the Functional-Segment Activity Coefficient Model: F-SAC

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Summary

1 Introduction

2 F-SAC

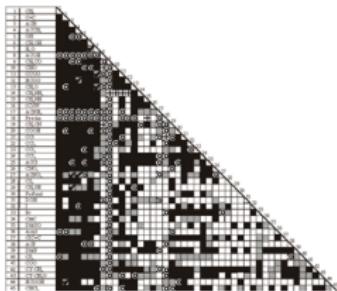
3 Conclusions



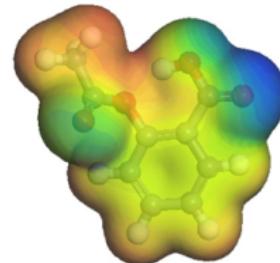
Two families of predictive activity coefficient (γ_i) models

- Group contribution models,
for instance:
- COSMO-RS like models, for
instance:

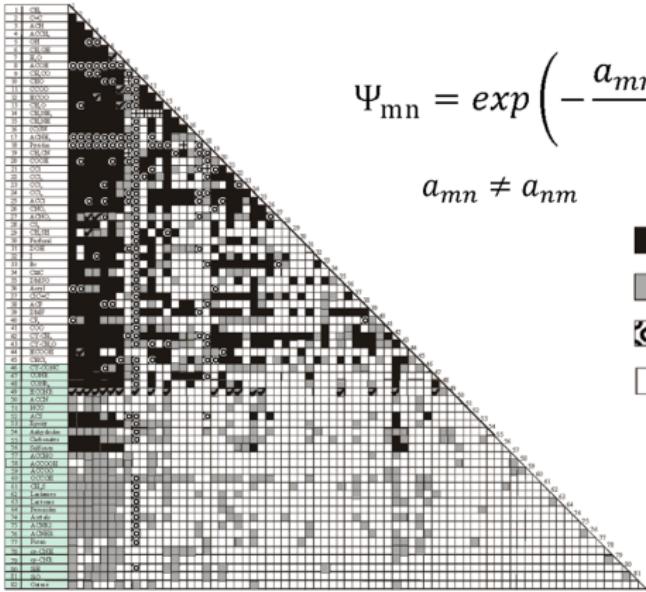
UNIFAC (Do)



COSMO-SAC



UNIFAC (Do) – Group Contribution



$$\Psi_{mn} = \exp\left(-\frac{a_{mn} + b_{mn}T + c_{mn}T^2}{T}\right)$$

$$a_{mn} \neq a_{nm}$$

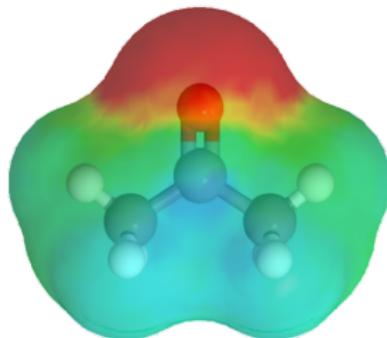
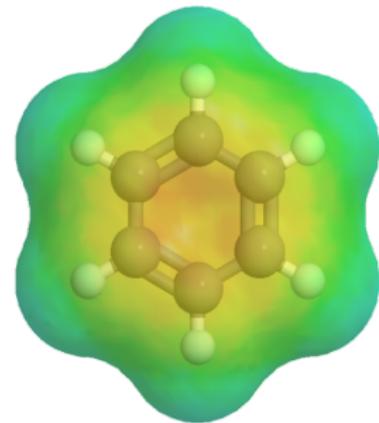
- published parameters
- consortium parameters
- revised parameters
- no parameters available



DOI:10.1021/ie060355c

According to revision 5 – Antje Jakob et al. In: *Ind. Eng. Chem. Res.* 45.23 (2006), pp. 7924–7933.

COSMO-RS – Surface contacting theory

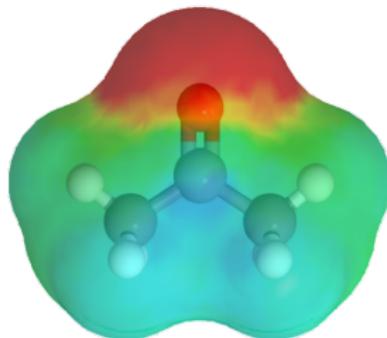
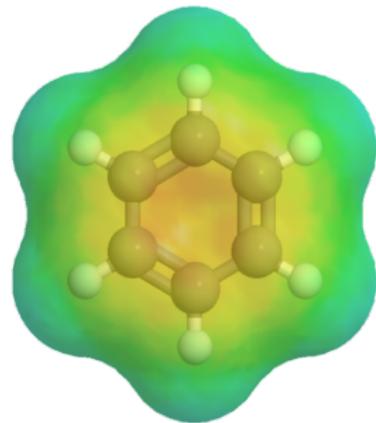


- First, for each insulated molecule the COSMO^a method is applied and the apparent surface charges are determined in a *cavity*
- Several approximations are considered here:
 - The cavity consists of spheres of fixed radii
 - Molecules surrounded by a perfect conductor
 - The methods used contains other approximations: AM1, RM1, DFT, MP2, etc.
 - The *escaping* charges need to be corrected
 - ...



^aA Klamt and G Schüürmann. In: *J. Chem. Soc., Perkin Trans. 2* (1993), pp. 799–805

COSMO-RS – Surface contacting theory

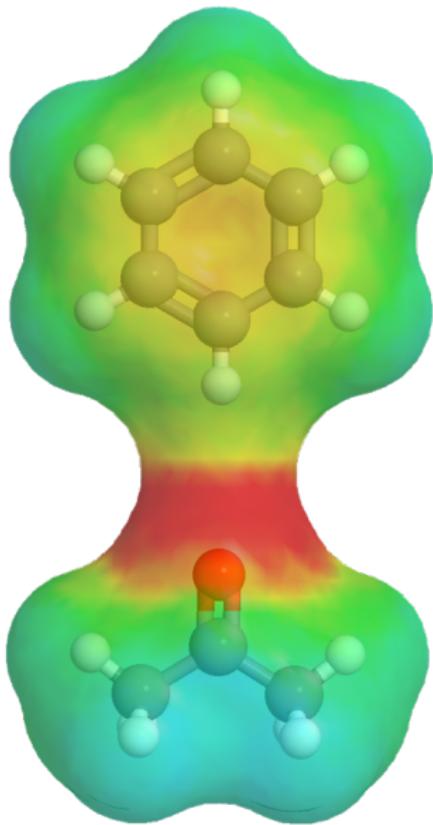


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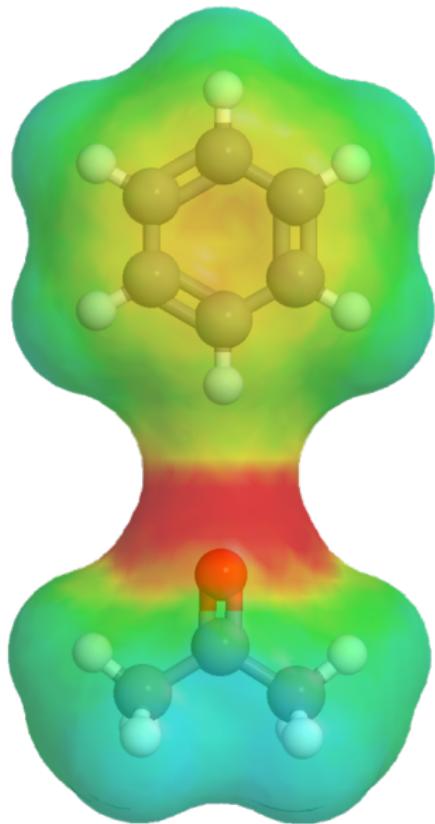


- In the COSMO-RS^a surface contacting theory, the molecules are sequentially put in contact
 - For each contact, the conductor is partially excluded
 - If each molecule is completely surrounded by others, the *real* solution would be obtained

^aAndreas Klamt. In: *The J. of Phys. Chem.* 99.7 (1995), pp. 2224–2235



COSMO-RS – Surface contacting theory

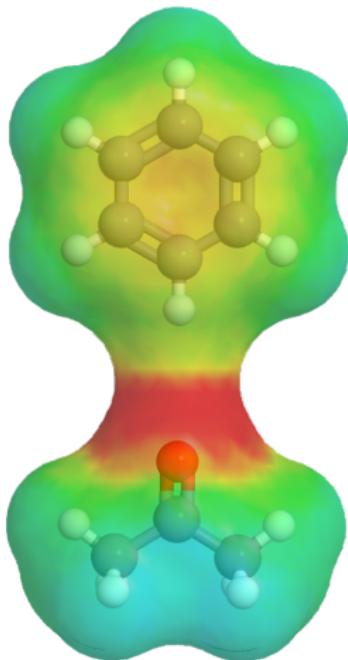


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COSMO-RS – Surface contacting theory

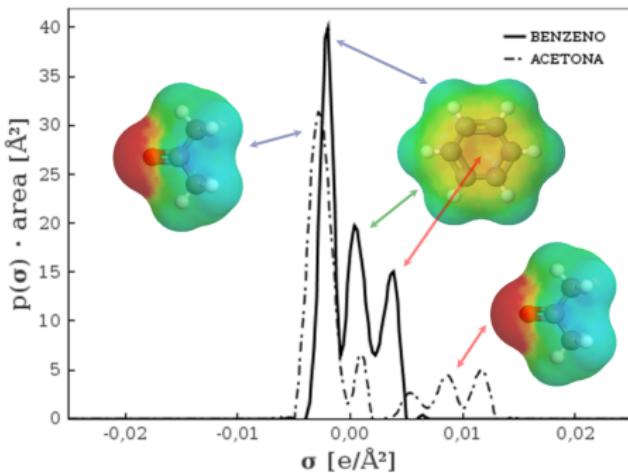


- For each surface pair contact, there is an energy change
- This results in different behavior for different substances in solution
- Clearly, there are many different possible contacting arrangements and *statistical thermodynamics* is necessary
- For the F-SAC model, the COSMO-RS variant known as COSMO-SAC^a is used

^aShiang-Tai Lin and Stanley I. Sandler. In: *Ind. Eng. Chem. Res.* 41.5 (2002), pp. 899–913



Sigma profile – $p(\sigma)$

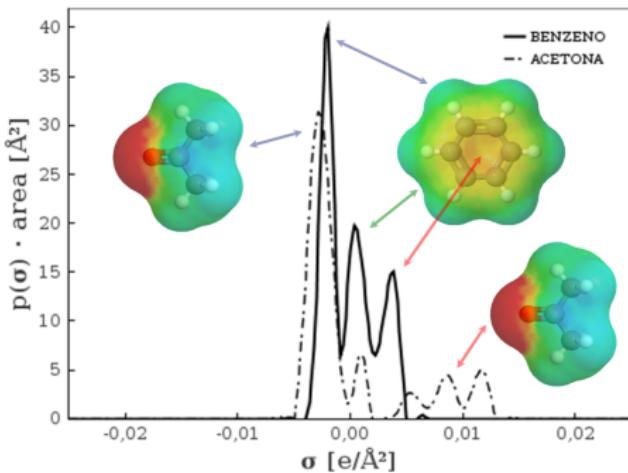


- For the statistical thermodynamics treatment, the 3D apparent surface charges are projected into a simple histogram
- These **pure compound** distributions, known as *sigma profiles* – $p(\sigma)$, are the basis for computing the activity coefficients in **mixture**

- "It is always desirable to express the properties of a solution in terms that can be calculated completely from the properties of the pure components." – J. M. Prausnitz. *Molecular thermodynamics of fluid-phase equilibria*. Third. Prentice-Hall, 1999.



Sigma profile – $p(\sigma)$

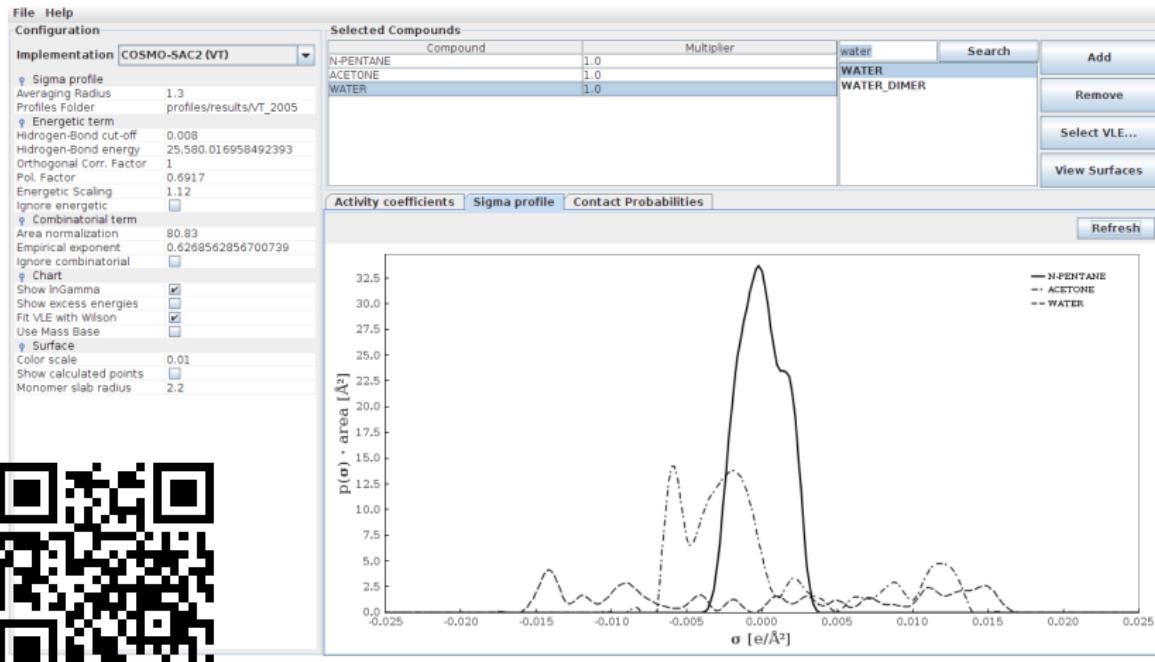


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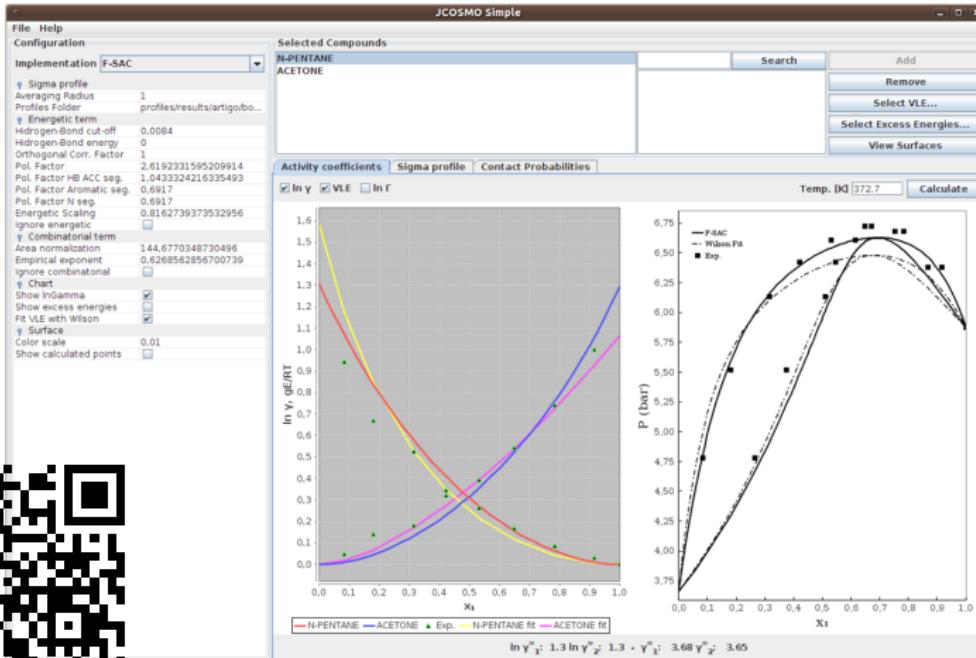
JCOSMO program: sigma profile of pure substances



code.google.com/p/jcosmo/



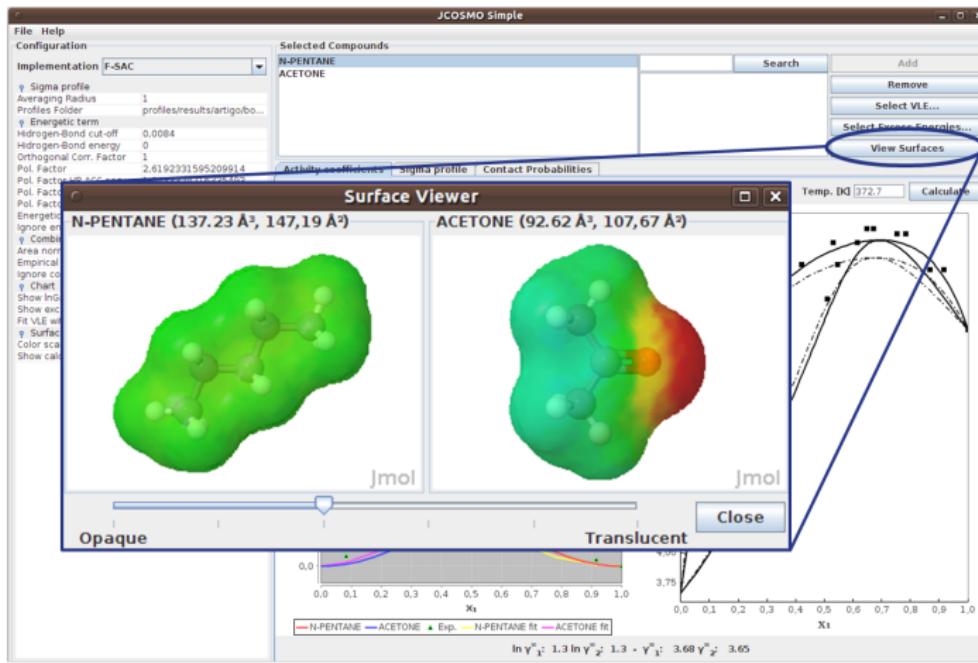
JCOSMO program: activity coefficient and VLE predictions



code.google.com/p/jcosmo/

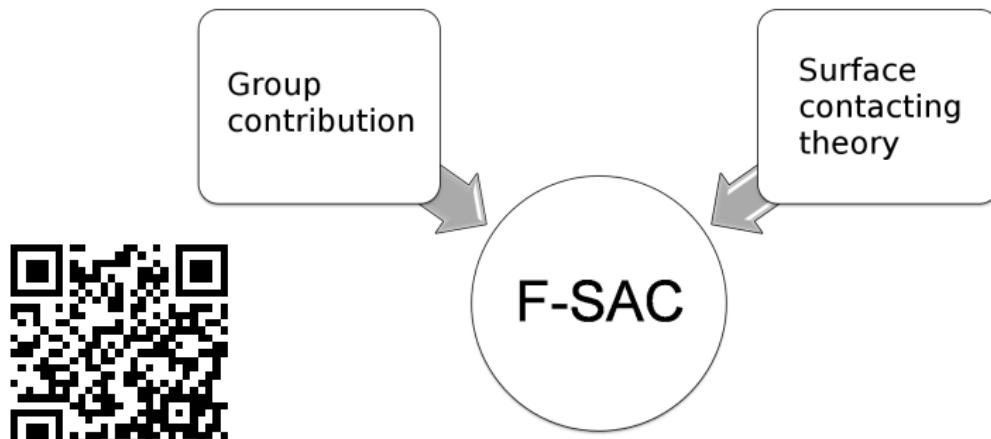


JCOSMO program: surface charges visualization



F-SAC: Motivation

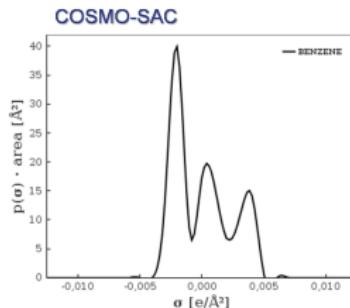
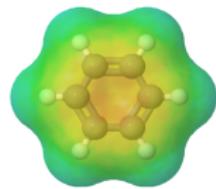
- Although COSMO-RS models have exceptional theoretical characteristics, in general quantitative experimental agreement is usually obtained by empirical modifications
- The F-SAC¹ model combines group contribution with the COSMO-RS theory:



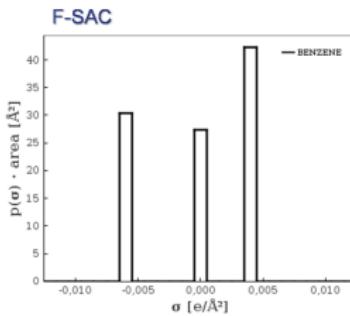
DOI:10.1021/ie400170a

¹R.P. Soares and R.P. Gerber. "Functional-Segment Activity Coefficient model. 1. Model formulation". In: *Ind. Eng. Chem. Res.* (2013). DOI: 10.1021/ie400170a.

Similarities/differences between COSMO-SAC and F-SAC

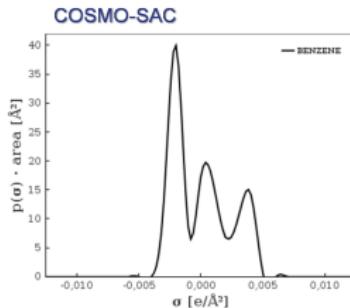
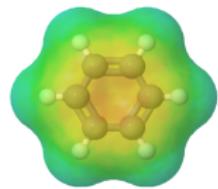


Exp.
Data

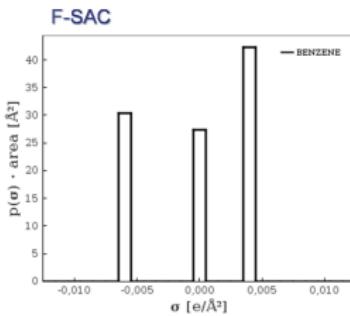


- The model equations are identical, the difference is in the sigma profile
- In the F-SAC model there is a neutral and two charged peaks per group

Similarities/differences between COSMO-SAC and F-SAC



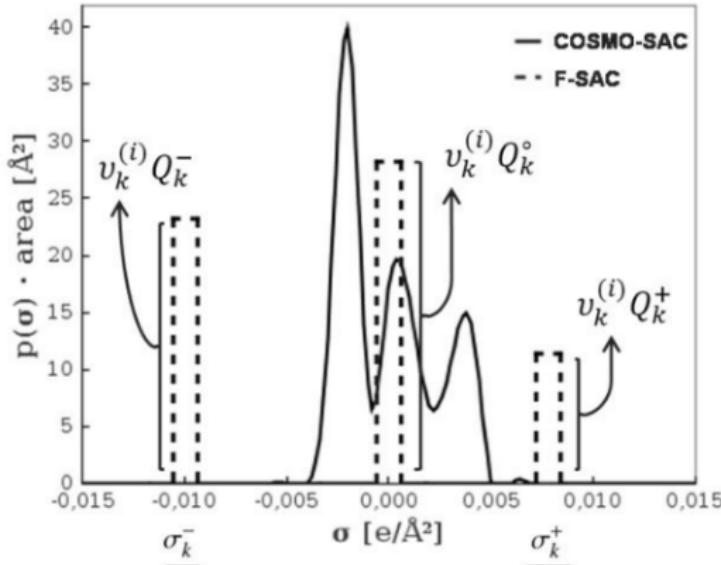
Exp.
Data



- The model equations are identical, the difference is in the sigma profile
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Sigma profiles from group contribution

$$p_i(\sigma) = \sum_k \nu_k^{(i)} p_k(\sigma)$$



DOI:10.1021/ie400170a



- Parameters to be calibrated based on experimental data for each group k :

Q_k total group surface area, initial value from COSMO computations²

Q_k^+ group positive area

Q_k^- group negative area

σ_k^+ surface charge density of the positive area portion

- Other parameters:

$Q_k^\circ = Q_k - Q_k^+ - Q_k^-$ group neutral area

$\sigma_k^- = \sigma_k^+ Q_k^+ / Q_k^-$ surface charge density of the negative area portion

²R.P. Gerber and R.P. Soares. In: *Braz. J. of Chem. Eng.* 30 (1 2013), pp. 1–11.

Parameter fit with experimental data

- Currently there are parameters for **24** functional groups divided in **48** subgroups³.
- The parameter estimation was accomplished using *Infinite Dilution Activity Coefficient* (IDAC) for more than 2000 mixtures at different temperatures.
- Additionally, VLE data for the ethanol/water system was also considered.

³R.P. Soares et al. "Functional-Segment Activity Coefficient model. 2. Associating Mixtures". In: *Ind. Eng. Chem. Res.* (2013). DOI: 10.1021/ie4013979.

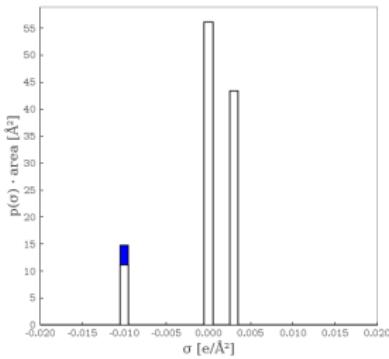
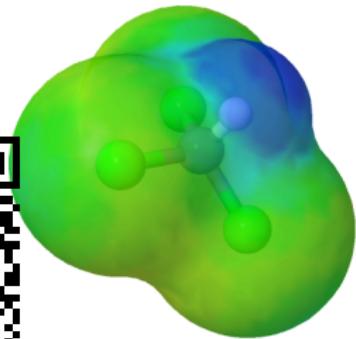
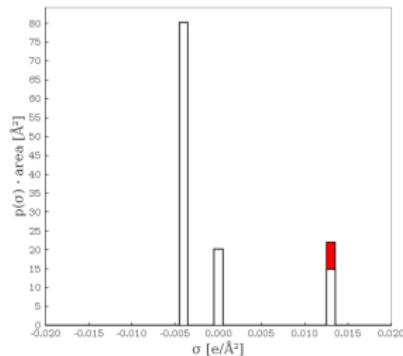
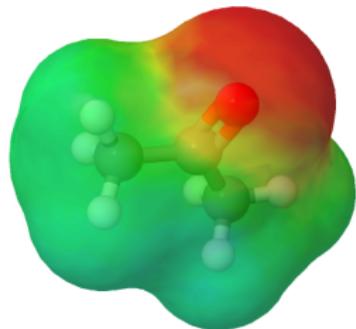
F-SAC parameters

- For the **24 grupos** considered, only **152** parameters were calibrated.
- Only the hydrogen-bonding* energies are **pairwise**
- All other parameters are for **pure** groups alone, reducing the total number of parameters
- In order to represent the same molecules in mixtures, **778** parameters are used in UNIFAC (Do).

Group	$Q_k^+/\text{\AA}^2$	$Q_k^-/\text{\AA}^2$	$\sigma_k^+/e \cdot \text{\AA}^{-2}$
CH_2	0.00	0.00	0.0000
C=C	6.16	3.70	0.0050
ACH	5.38	6.71	0.0056
CH_3COCH_3	21.97	80.23	0.0133
CH_2CHO	14.85	81.88	0.0172
CH_3COAC_3	9.56	16.68	0.0162
c- CH_2COCH_2	13.93	42.78	0.0166
$\text{CH}_3\text{COOCH}_3$	28.94	107.69	0.0109
Triacetin	34.68	62.83	0.0146
GBLactone	18.05	41.30	0.0161
Phthalate	33.60	69.26	0.0132
$\text{CH}_2\text{COOAC}_3$	12.59	64.23	0.0158
CH_3OCH_2	13.01	22.71	0.0091
c- CH_2OCH_2	8.12	27.20	0.0143
$\text{N}(\text{CH}_2)_3$	3.60	28.58	0.0175
DMSO	11.36	22.84	0.0188
CH_2Cl	9.30	9.07	0.0089
CCl_4	18.40	26.23	0.0062
CH_3CCl_3	40.07	20.28	0.0039
CHCl_3	43.32	14.76	0.0035
CIAC_3	37.41	12.13	0.0026
CH_3OH^*	8.31	4.72	0.0132
CH_2OH^*	7.34	4.69	0.0145
H_2O^*	8.84	12.16	0.0123

F-SAC parameters for Hydrogen-Bonding mixtures

HB-acceptor is red (positive), HB-donor is blue (negative).



DOI:10.1021/ie401397g

F-SAC parameters for Hydrogen-Bonding mixtures

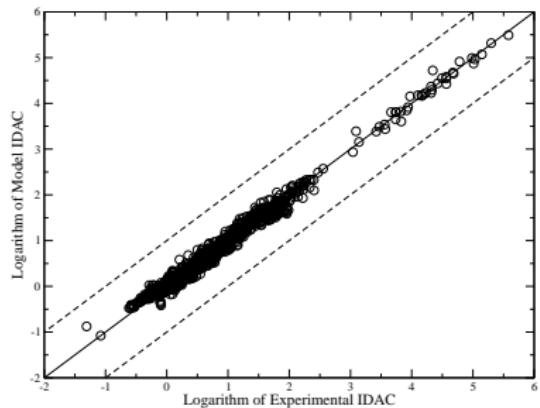
- Only the hydrogen-bonding energies are **pairwise^a**
- All other parameters are for **pure** groups alone
- All F-SAC parameters have a physical meaning, e.g. the estimated F-SAC water HB energy is 21.84 kJ/mol and it should be^b in the range of 20.4 to 23.3 kJ/mol.

Donor	Acceptor	$E^{\text{HB}}/\text{kJ}\cdot\text{mol}^{-1}$
CHCl ₃	ACH	1.76
	CH ₃ COCH ₃	3.64
	CH ₃ COOCH ₃	7.68
	CH ₃ OCH ₂	12.53
	CH ₃ OH	8.63
	CH ₂ OH	8.22
	ACH	0.90
	CH ₃ COCH ₃	19.44
	CH ₃ COOCH ₃	21.90
	CH ₃ OCH ₂	23.90
H ₂ O	CH ₃ OH	24.04
	CH ₂ OH	22.58
	H ₂ O	21.84

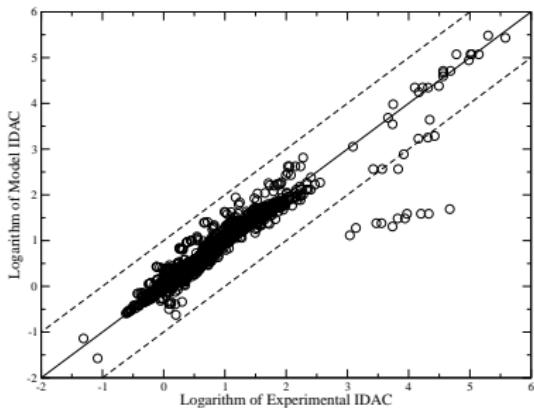
^aR.P. Soares et al. "Functional-Segment Activity Coefficient model. 2. Associating Mixtures". In: *Ind. Eng. Chem. Res.* (2013). DOI: 10.1021/ie4013979

^bK. Wendler et al. In: *The J. of Phys. Chem. A* 114.35 (2010), pp. 9529–9536

IDAC comparison for non-associating mixtures



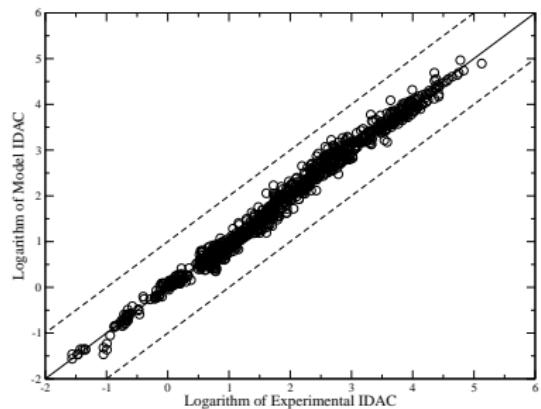
(e) F-SAC



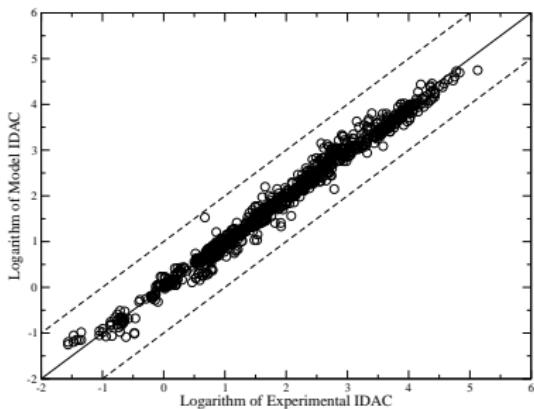
(f) UNIFAC (Do)



IDAC comparison for associating mixtures (water excluded)



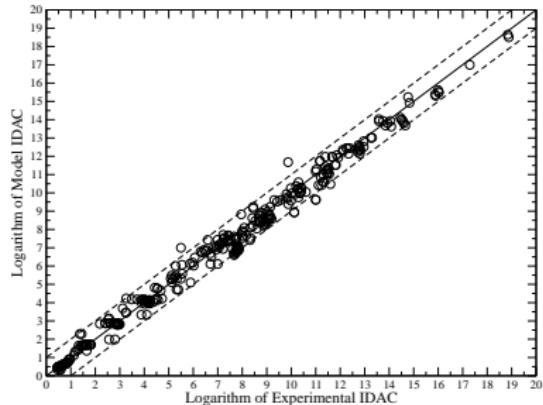
(g) F-SAC



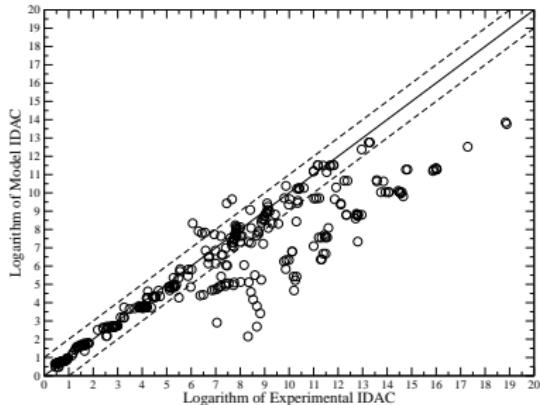
(h) UNIFAC (Do)



IDAC comparison for aqueous mixtures



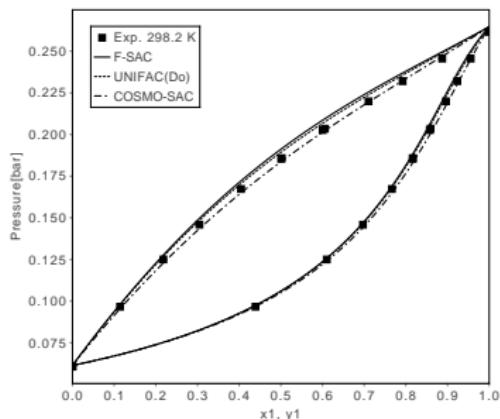
(i) F-SAC



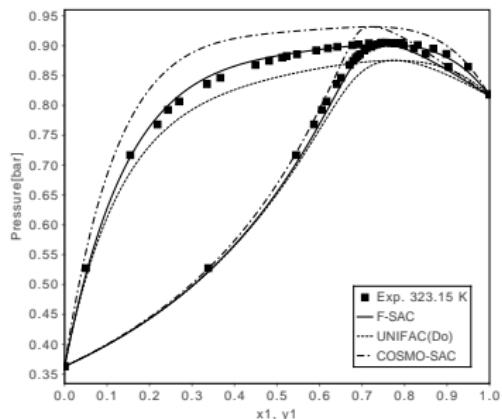
(j) UNIFAC (Do)



VLE predictions for non-associating mixtures



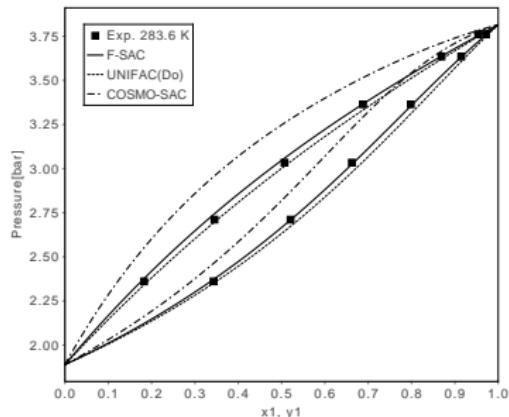
(k) Chloroform/n-heptane



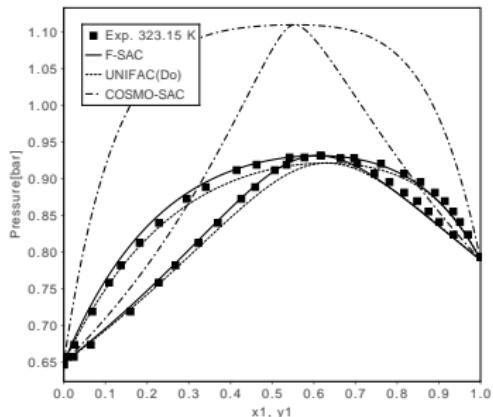
(l) Acetone/cyclohexane



VLE predictions for non-associating mixtures



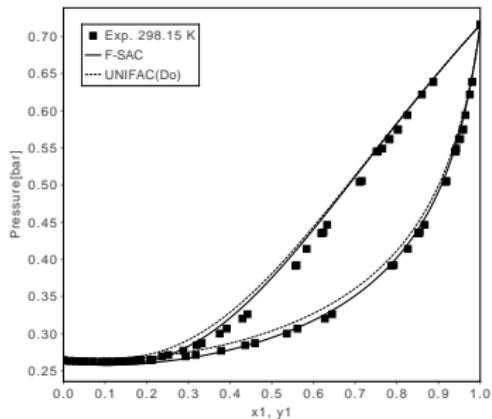
(m) Dimethyl ether/1-butene



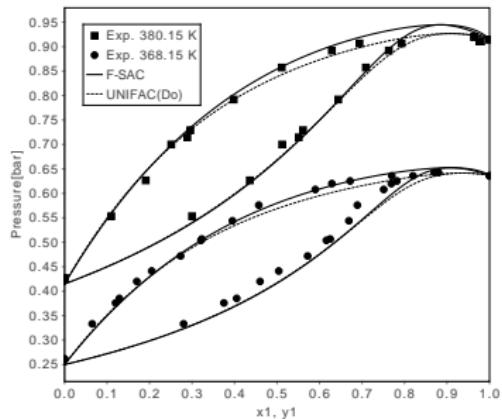
(n) Methyl acetate/1-hexene



VLE predictions for associating mixtures



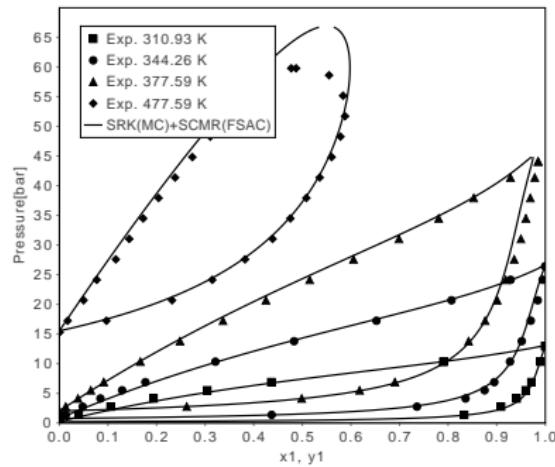
(o) diethyl-ether/chloroform



(p) toluene/3-methyl,1-butanol

Predicting high-pressure VLE with SCMR

- SRK with Mathias-Copeman α function and the Self-Consistent Mixing Rule⁴ (SCMR) for propane-benzene, no parameter is adjusted for the mixture effects:



⁴Paula B. Staudt and Rafael de P. Soares. In: *Fluid Phase Equilibria* 334 (2012), pp. 76–88.

Possible representations for IL

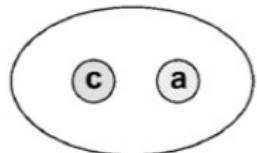
- According to the literature⁵, one of the following:

Meta-file: the IL is considered a single compound, the σ -profile is given by the **sum** of ions \Leftarrow

Ion-pair: COSMO computations with the ion-pair

Electroneutral mixture: independent ions in mixture in equimolar proportion

Meta file approach



Ion pair



Electroneutral mixture

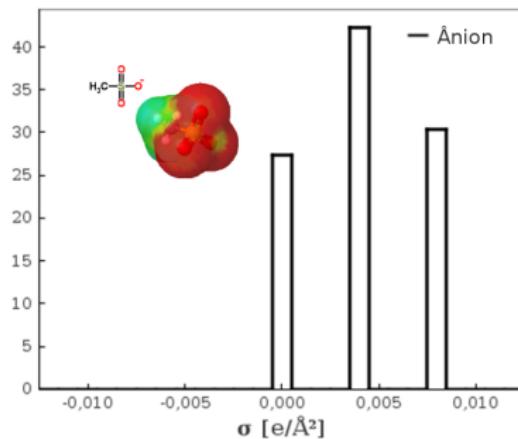
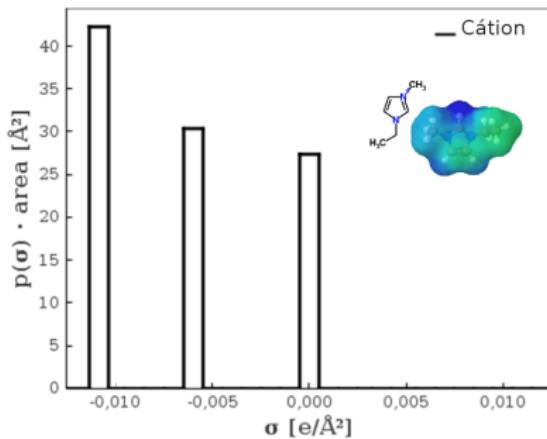


50:50

⁵M. Diedenhofen and A. Klamt. In: *Fluid Phase Equilib.* 294.1-2 (2010), pp. 31–38.

F-SAC: formulation for IL

- We have selected the **meta-file approach** for F-SAC: cations and anions are the functional groups and the IL σ -profile is given by the groups addition:



F-SAC: parameters for charged groups

- The number of independent parameters per group is the same:

Q_k^a first charged peak

Q_k^b second charged peak

σ_k^a charge density of the first peak

- The other parameters are:

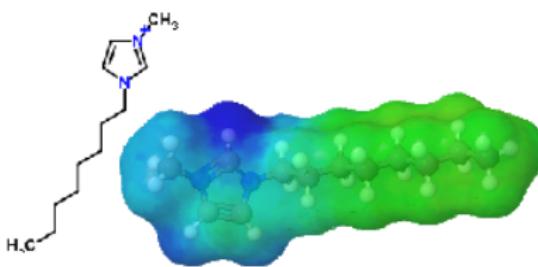
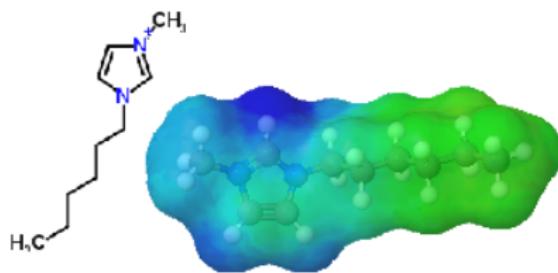
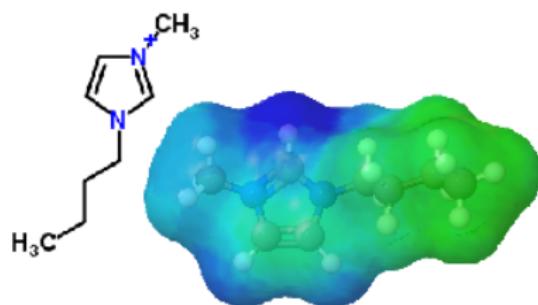
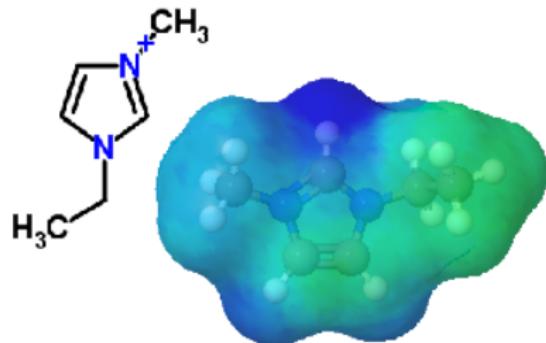
z group charge (+1, -1, etc.)

$Q_k^\circ = Q_k - Q_k^a - Q_k^b$: neutral area

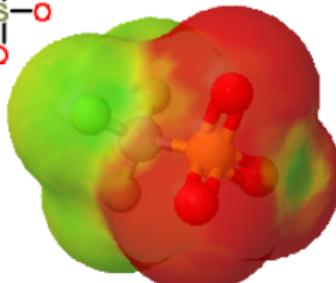
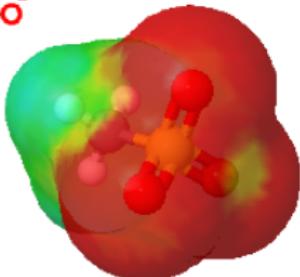
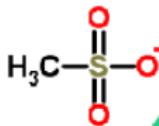
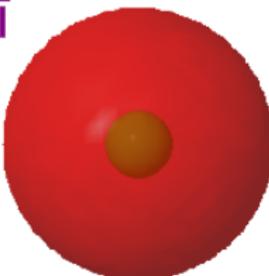
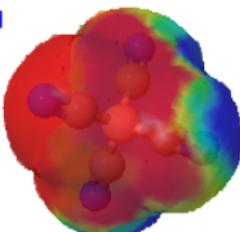
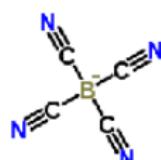
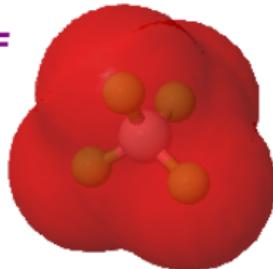
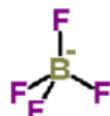
$\sigma_k^b = (z/Q_k - \sigma_k^a Q_k^a)/Q_k^b$: charge density of the second peak



Cations selected for the first study



Anions selected for the first study



IL tested

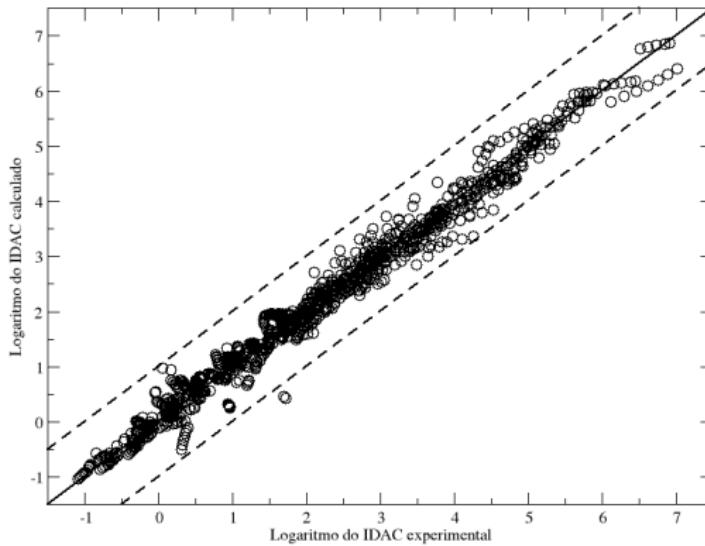
- A databank was assembled with 1031 mixtures with 9 different IL:

[EMIM]⁺[BF₄]⁻
[BMIM]⁺[BF₄]⁻
[HMIM]⁺[BF₄]⁻
[OMIM]⁺[BF₄]⁻
[EMIM]⁺[TCB]⁻
[HMIM]⁺[TCB]⁻
[OMIM]⁺[CL]⁻
[EMIM]⁺[MESO₃]⁻
[EMIM]⁺[CF₃SO₃]⁻



IDAC of 1031 mixtures (substances dissolved in IL)

- The average deviation was **0,17** ln units, similar to the observed for the neutral mixtures



Conclusions

- **F-SAC** is a new group contribution model
- Its mathematical formulation is more complex (COSMO-RS based), but it requires less parameters (and experimental data) than UNIFAC
- When correlating a diverse IDAC database for non associating mixtures, the F-SAC correlation deviated from experimental data by **0.073** ln units against **0.14** for UNIFAC (Do) predictions
- For aqueous mixtures the F-SAC correlation deviated by **0.338** while the UNIFAC (Do) predictions deviated by **1.23**
- Good predictions were also obtained for VLE data, not included in the parameter fitting process



Ongoing research

- The F-SAC model is currently being revised and extended
- The number of groups is being extended
- Now we are also considering VLE and LLE data in the parameter estimation process for improved parameter quality
- Improved formulations for associating mixtures (hydrogen bonds) are being tested
- Applications for polymer systems are being investigated
- Parameters for light gases are being calibrated by means of **CEO_s/GE** mixing rules



Thank you!

- Download F-SAC demonstration code at
<http://www.enq.ufrgs.br/lvpp>
- Download the JCOSMO program, including source code, at
<http://code.google.com/p/jcosmo/>



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