Property Prediction of Ionic Liquid Solutions Using Cosmo-RS

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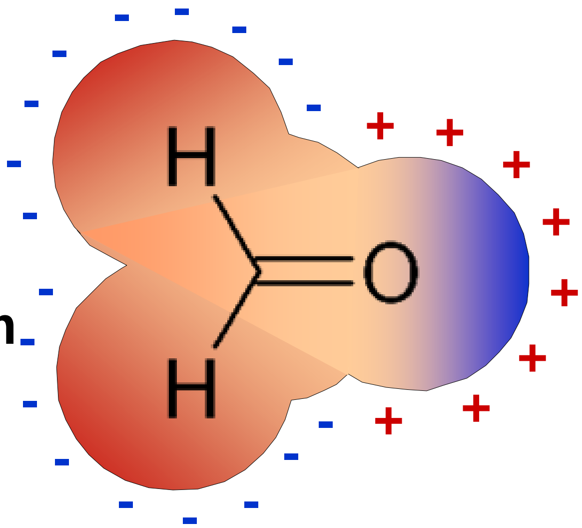
Outline

- Introduction: COSMO / COSMO-RS
- Technical Details of IL calculations
- Prediction of activity coefficients of solutes in ILs
- LLE predictions
- Prediction of IL vapor pressures

Some definitions

Theory	Implementation
COSMO-RS *the physical model*	**COSMO*therm*** *the COSMO-RS implementation*
COSMO the **Co**nductorlike **S**creening **Mo**del *the Quantum Chemistry (QC) method*	**QC packages** *(DMOL, TURBOMOLE, ADF, GAMESS, GAUSSIAN, MOLPRO, PQS,ORCA…)*

Dielectric continuum solvation models

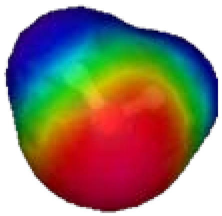


Concept for describing compounds in solution:

- **Simulations using explicit solvent molecules**
- **Embed the molecule in a dielectric continuum**

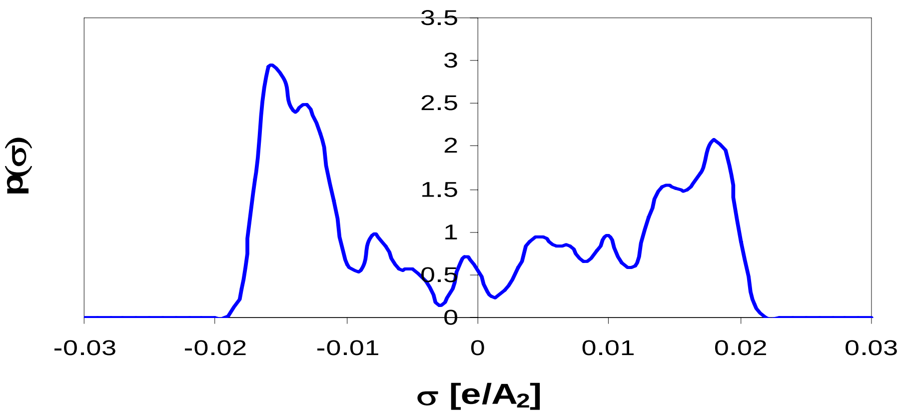
- COSMO: $\mathbf{\Phi}^{tot} = 0 \longrightarrow \mathbf{q} = -\mathbf{A}^{-1}\mathbf{\Phi}^{sol}$

$$\sigma_i = \frac{q_i}{a_i} \longrightarrow$$

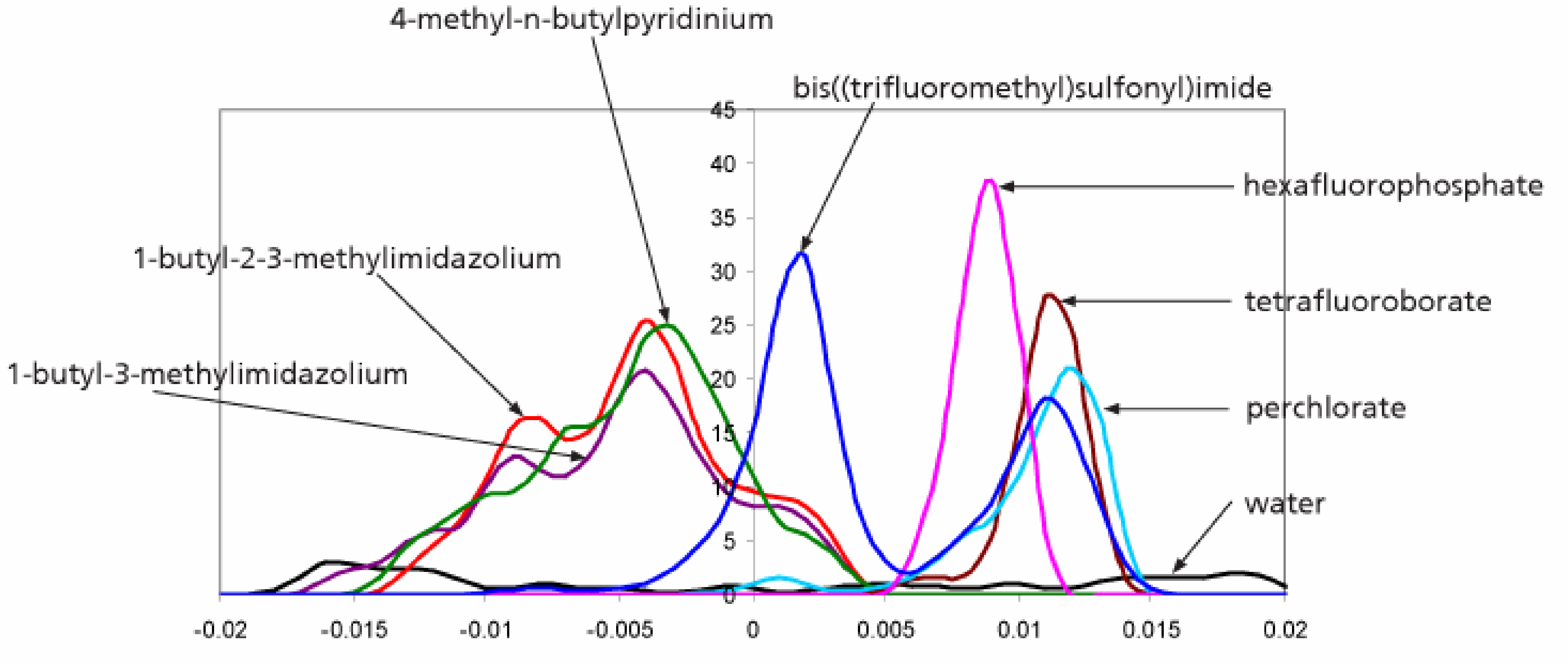


$\longrightarrow$

"σ-profile" p(σ) of Water



σ-profiles of some ILs



COSMO-RS

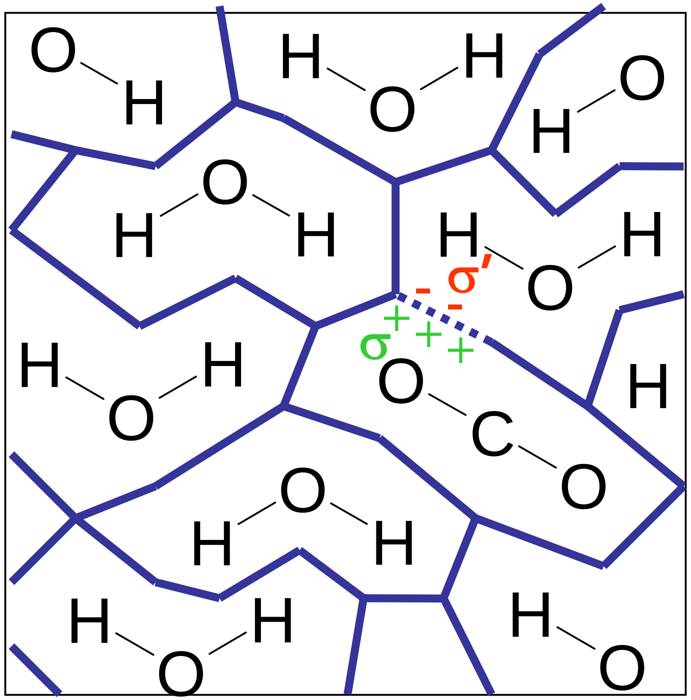
- **All surfaces are assumed to be in close contact.**

- **If screening charges σ and σ ' on surface pairs differ, an interaction energy will result from the "*misfit*" of these charges.**

adjustable parameter

$$E_{Misfit}(\sigma,\sigma') = \frac{\alpha'}{2}(\sigma+\sigma')^2$$

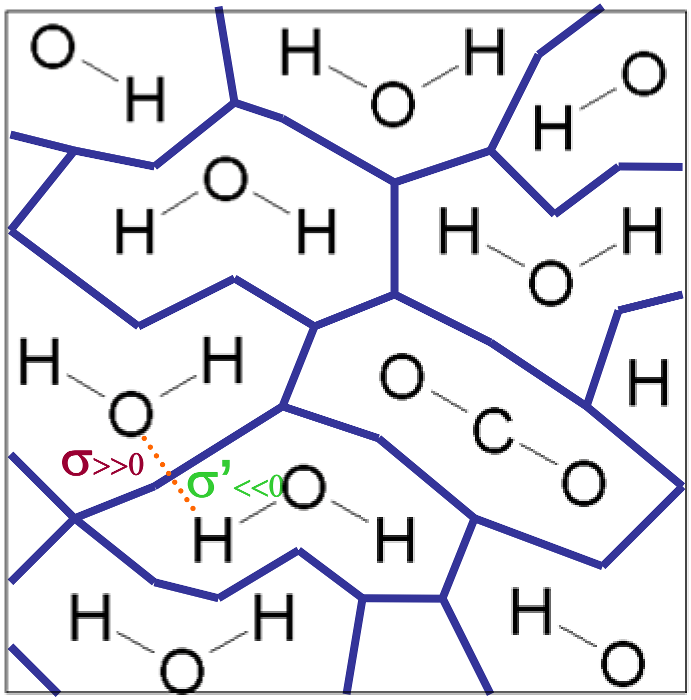
E_{Misfit} describes electrostatic interactions between molecular surface parts of different polarity.



COSMO-RS

Two additional interactions are incorporated into the COSMO-RS model:

- **Hydrogen bond interactions between surface pieces of strongly different polarity σ << 0 and σ' >> 0**:



adjustable parameter

$$E_{HB}(\sigma,\sigma') = \max\{0, -c_{HB}(\sigma\cdot\sigma' + \sigma_{HB}^{2})\}$$

- **Spatially non-specific van der Waals interactions:**

$$E_{vdW} = g_{vdW} + g'_{vdW}$$

g_{vdW} are element specific adjustable parameter

- **COSMO-RS interaction energy**: $E_{\text{int}} = E_{Misfit} + E_{HB} + E_{vdW}$

COSMO-RS

- **The ensemble S is fully characterized by the "σ-profiles".**

$$P_S(\sigma) = \sum_{i \in S} x_i P^i(\sigma)$$

- **Chemical potential of a surface segment***

Iterative solution

$$\mu_S(\sigma) = -kT \ln \int p_S(\sigma') \exp\left\{ -\frac{E_{int}(\sigma,\sigma') - \mu_S(\sigma')}{kT} \right\} d\sigma'$$

- **The "σ-potential" $\mu_S(\sigma)$ is a measure for the affinity of system S to a surface of polarity σ.**

- **The chemical potential of component X in system S is calculated by**

$$\mu_S^X = \int p^X(\sigma) \mu_S(\sigma) d\sigma + \mu_{C,S}^X$$

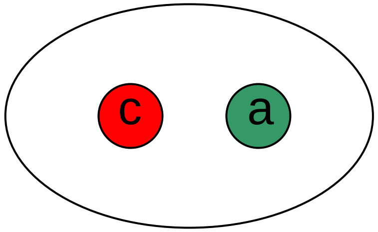
combinatorial term (size & shape effects)

* F. Eckert, A. Klamt, *AIChE Journal*, 48 (**2002**) 369-385. A. Klamt, J. Phys. Chem., 99 (**1995**) 2224.

Technical Details of IL Calculations

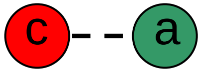
Meta file approach

IL treated as one compound (sum of sigma profiles, areas, and volumes of the ions)



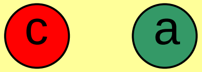
Ion Pair

The ion pair calculated on the COSMO level



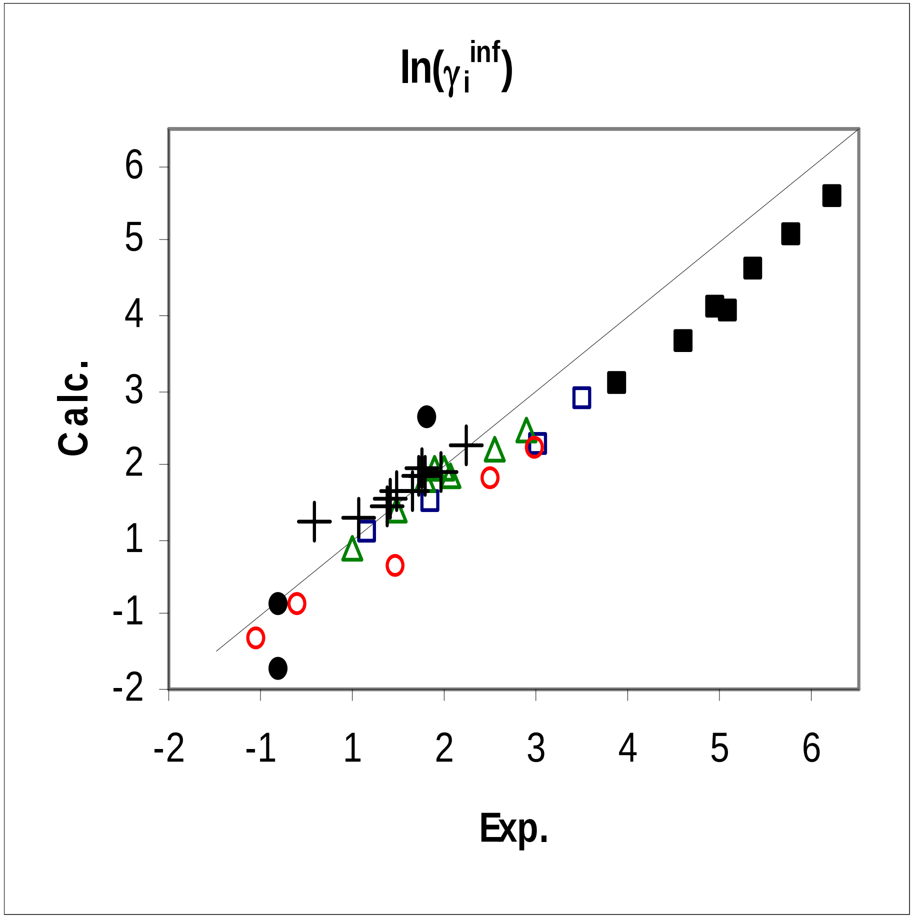
Equimolar mixture of the two ions

The ions are treated like two different compounds



50:50

Activity Coefficients at Infine Dilution in $[bmpy][BF_4]$ at 314 K



Alkanes (■)
Alkenes (□)
Alkylbenzenes (Δ)
Alcohols (+)
Polar Organics (○)
Chloromethanes (●)

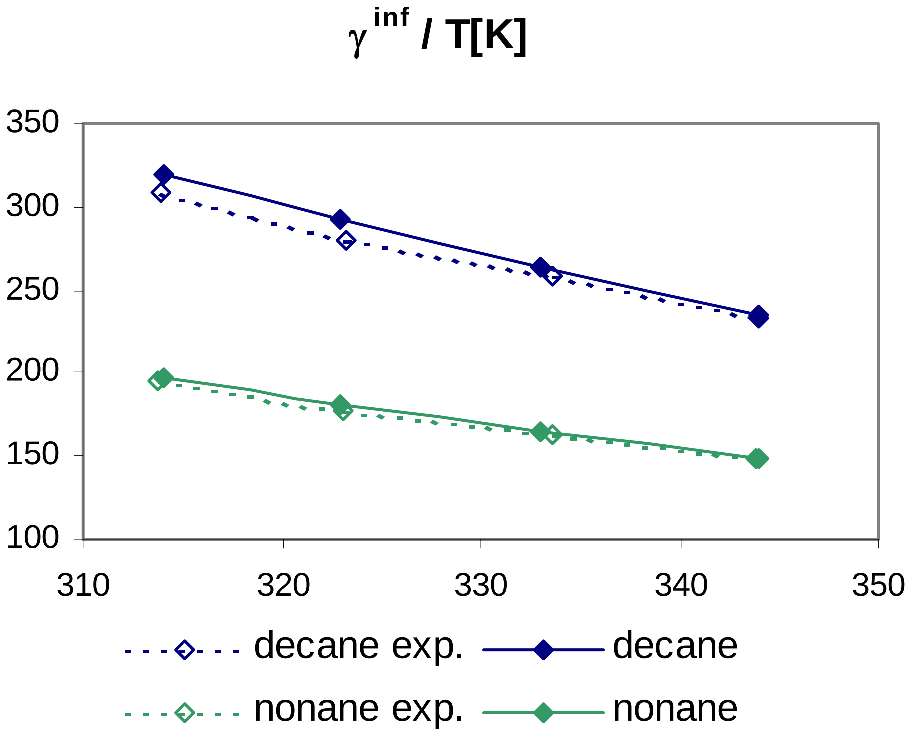
RMS: 0.524 ln-units

M. Diedenhofen, F. Eckert, and A. Klamt, *J. Chem. Eng. Data*, 2003, 48, 475-479

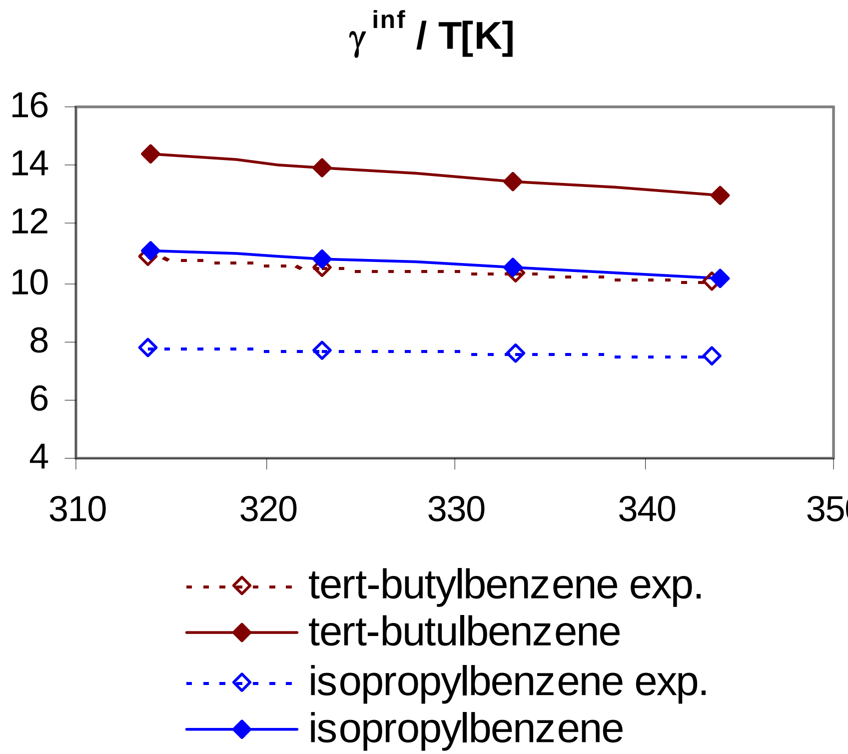
Exp. data: A. Heintz, D. V. Kulikov, S. P. Verevkin, *J. Chem. Eng. Data* 2001, 46, 1526-1529.

Temperature Dependence of γ^{inf}

Alkanes



Aromatic Compounds



Activity Coefficients at Infinite Dilution (all Solutes)

ln(γ^{inf}) Deviations from Exp. Data[3] (all Temp. and Solutes)

IL	RMS	Data Points	Max. Deviation
[bmim][$N(SO_2CF_3)_2$]	0.29	52	0.60 (heptane, 20°C)
[emim][$N(SO_2CF_3)_2$]	0.31	80	0.78 (heptane, 20°C)
[N-ethylpyridinium][$N(SO_2CF_3)_2$]	0.40	122	1.02 (octane, 30°C)
[mmim][$N(SO_2CF_3)_2$]	0.51	54	1.11 (heptane, 30°C)
[pyridinium][$C_2H_5OC_2H_4OSO_3$]	0.91	56	1.42 (1-pentene, 50°C)
[ocmim][Cl]	0.93	45	1.30 (pentane, 25°C)
[emim][$C_2H_5OSO_3$]	1.21	42	1.74 (heptane, 30°C)
[mmim][$CH_3OC_2H_4OSO_3$]	1.51	56	2.26 (1-heptene, 40°C)
[mmim][CH3OSO_3]	1.55	56	2.34 (1-heptene, 30°C)
[mmim][$(CH_3O)_2PO_2$]	1.66	59	2.96 (1-octene, 30°C)

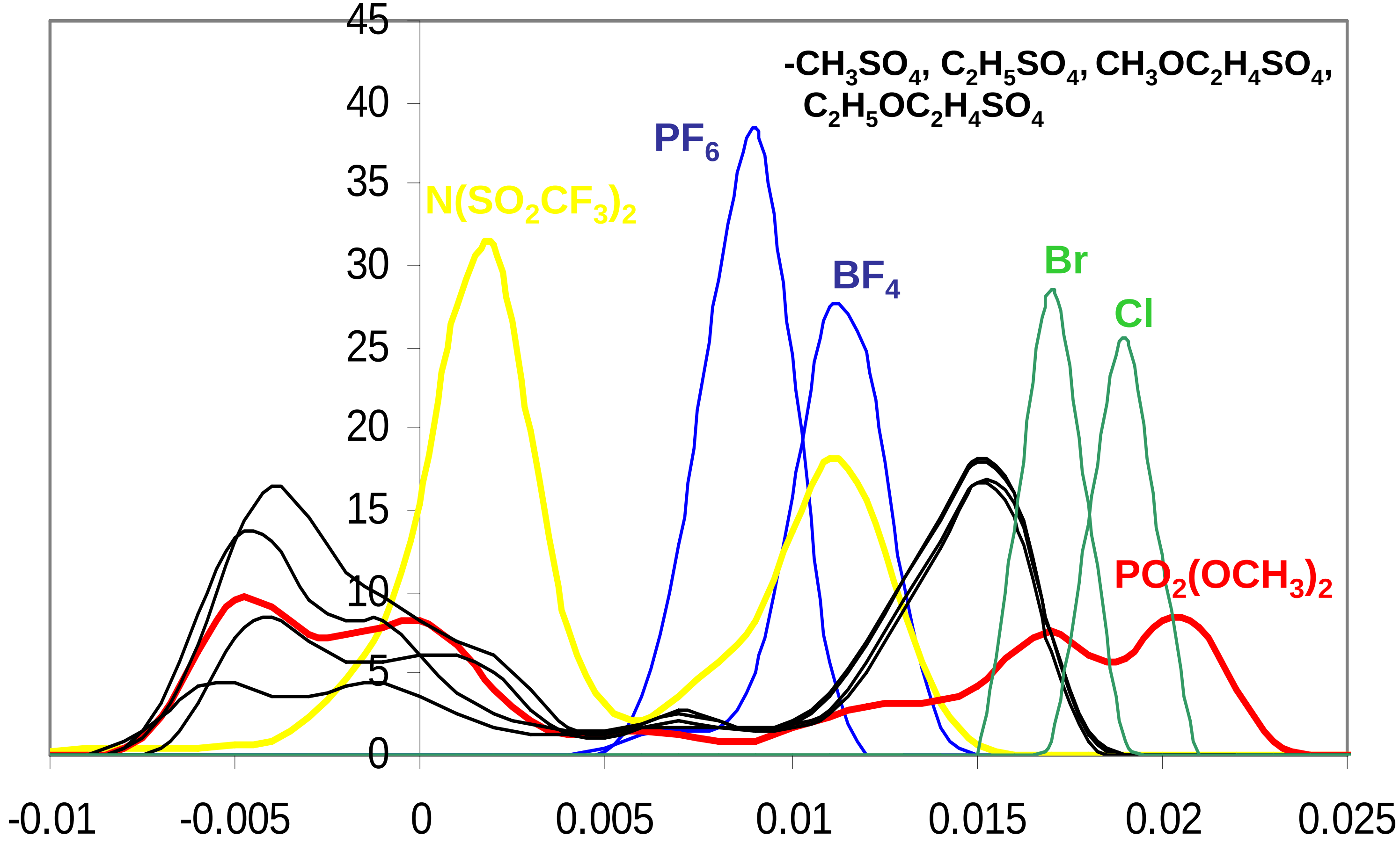
Exp. Data:

a) R.Kato, J. Gmehling, Fluid Phase Equilibria 226 (2004), 37-44

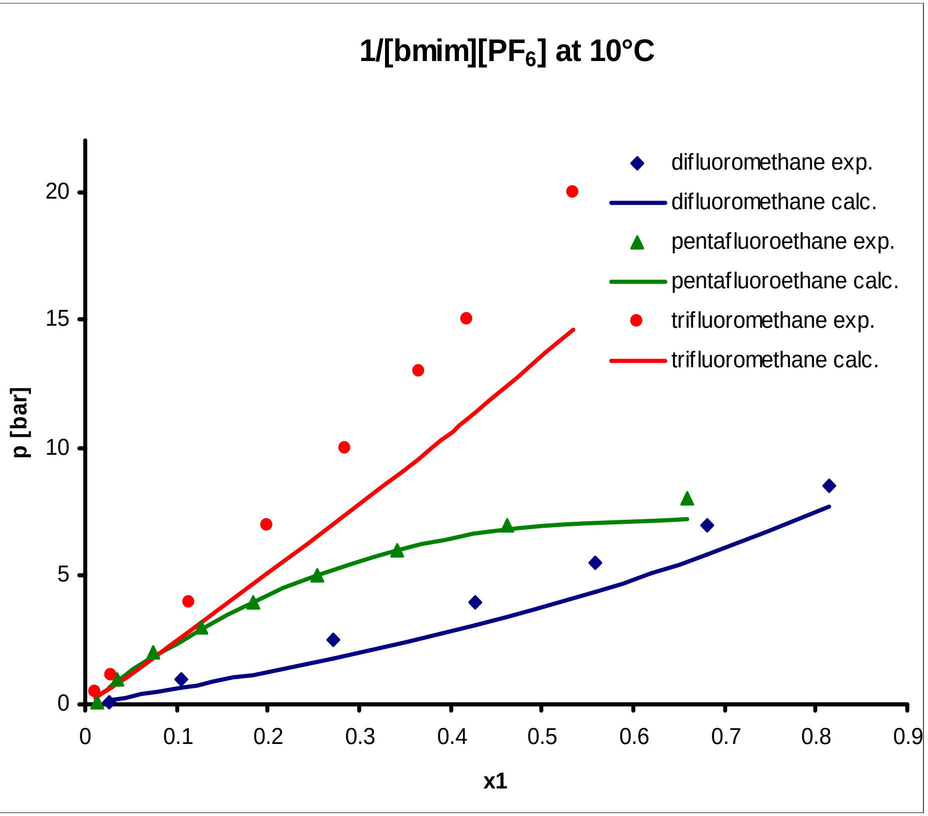
b) M. Krummen, P. Wasserscheid, J. Gmehling, J. Chem. Eng. Data 47 (2002), 1411-1417.

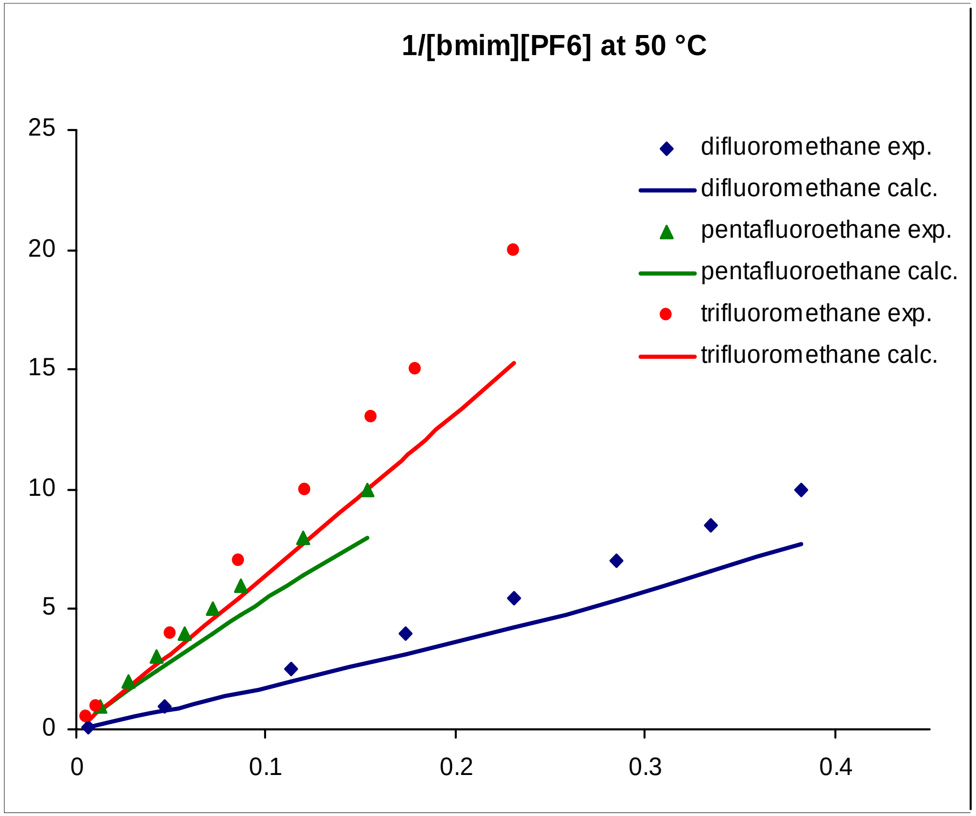
c) W. David, T. M. Letcher, D. Ramjugernath J. D. Raal, J. Chem. Thermodynamics 35 (2003),1335-1341.

σ-profiles of some IL Anions



VLEs of Fluoroalkanes in $[bmim][PF_6]$

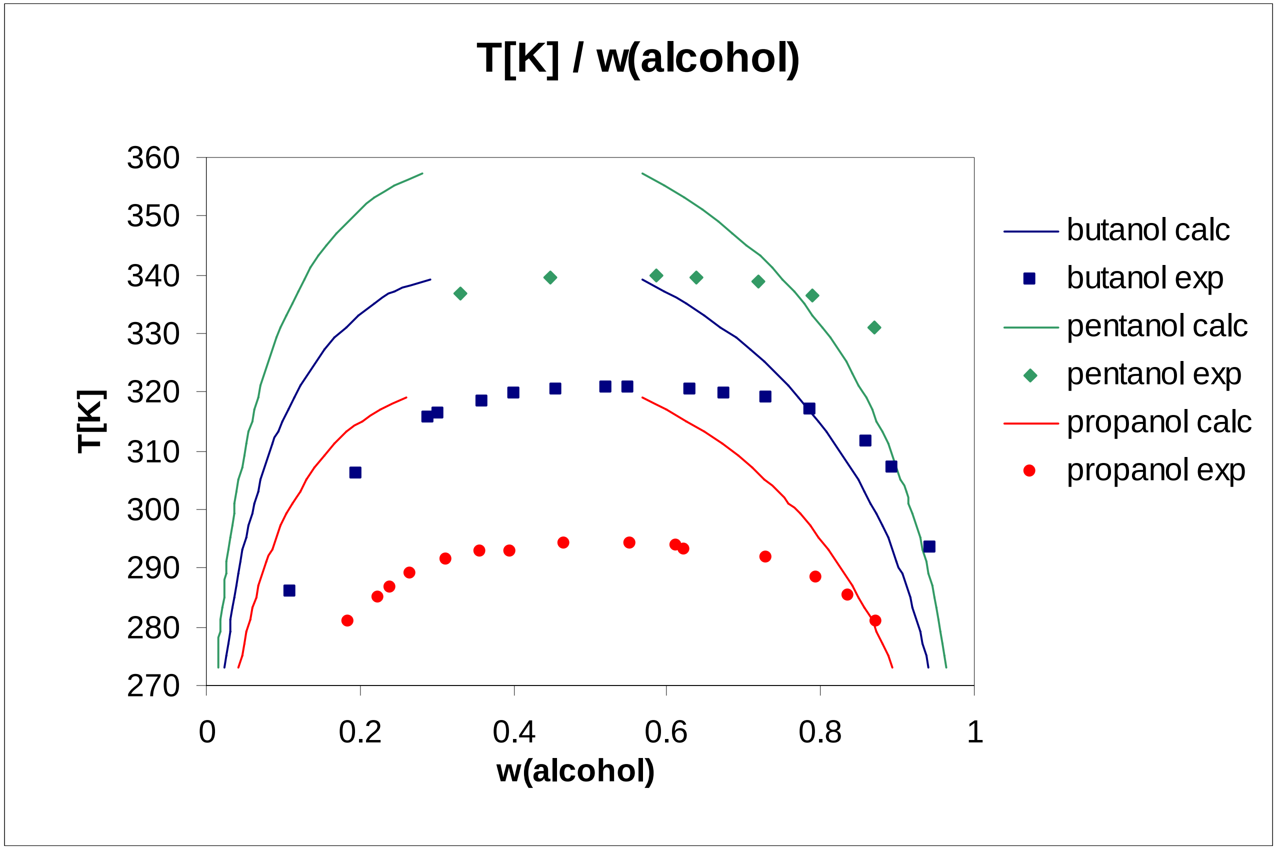




Exp. data from:

Mark B. Shiflett and A. Yokozeki, Solubility and Diffusivity of Hydrofluorocarbons in Room-Temperature Ionic Liquids, AIChE Journal, 52, 1205 (2005).

LLE Predictions of Alcohols in [emim][NTf_2]

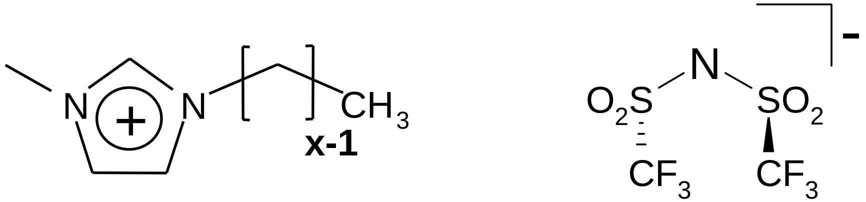


Exp. data: Heintz, A.; Lehmann, J. K.; Wertz, C.; J. Chem. Eng. Data; (Article); 2003; 48(3); 472-474.

Parameterization BP_TZVP_C12_0402.ctd

Vapor Pressure of [C_xMIM] [NTf2]

n-alkyl-3-methylimidazolium-*bis*-(trifluoromethanesulfonyl) amide



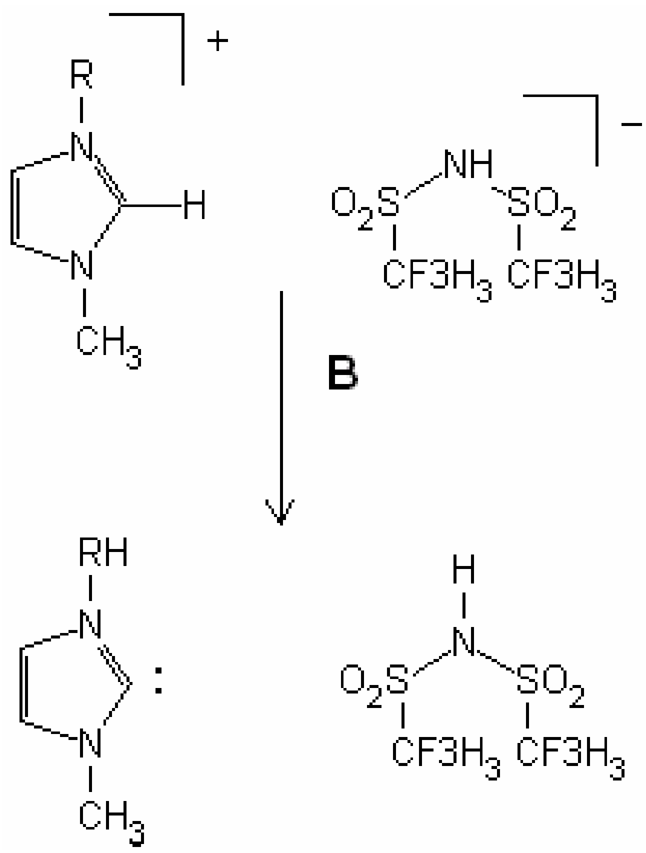
M. Diedenhofen, A. Klamt, K. Marsh and A. Schäfer
Phys. Chem. Chem. Phys., 2007, 9, 4653 - 4656

Experimental work:

Dz. H. Zaitsau, G. J. Kabo, A. A. Strechan, Y. U. Paulechka, A. Tschersich, S. P. Verevkin, and A. Heintz, *J. Phys. Chem. A*, 2006, 110, 7303-7306

Y. U. Paulechka, Dz. H. Zaitsau, G. J. Kabo, and A. A. Strechan, *Thermochimica Acta*, 2005, 439, 158-160.

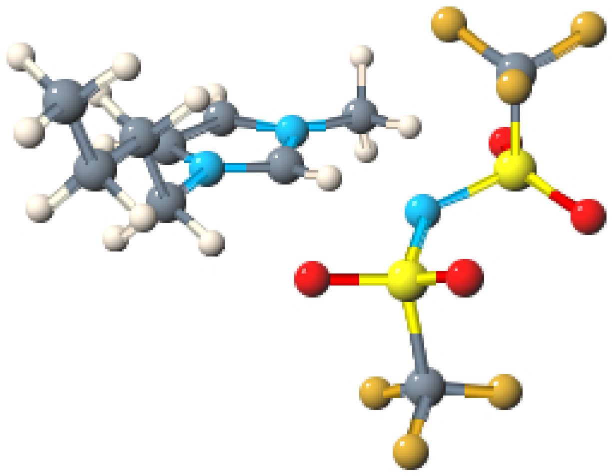
Neutralization Pathways



ΔG_{react} [kJ mol^{-1}] for R=butyl (T=437.8 K)
BP/TZVP

Path A: -251.0
Path B: -154.7

Optimized Structure of [BMIM][NTf_2]

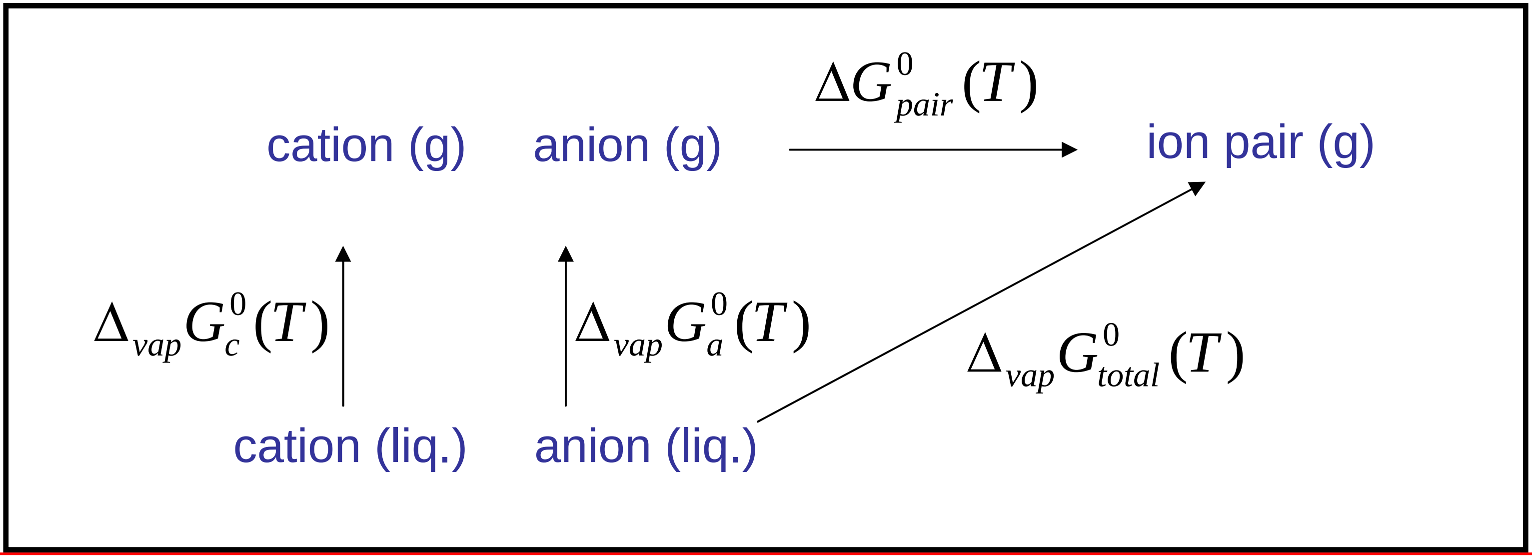


Calculation of the Vapor Pressure (Approach I)

$$\ln\left(p(T) \big/ P^0 \right) = -\frac{\left[\Delta_{vap} G_c^0(T) + \Delta_{vap} G_a^0(T) + \Delta G_{pair}^0(T) \right]}{RT}$$

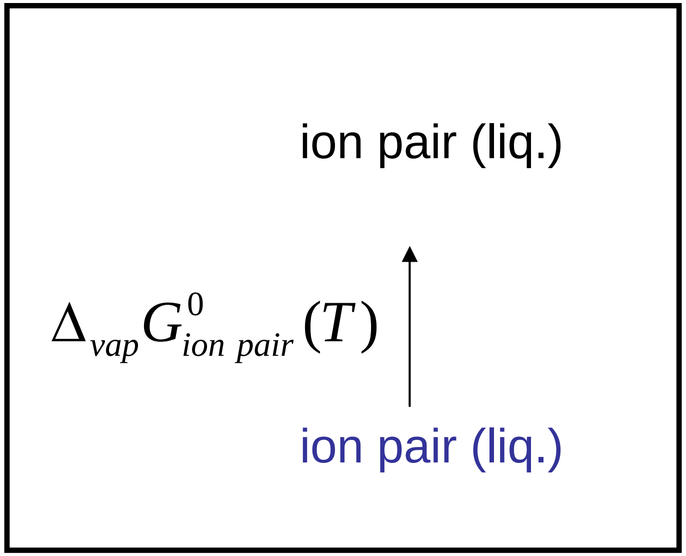
Gibbs energy of
cat/an-ion vaporization
calculated from the 50:50 cation/anion
mixture

Gibbs energy of the
neutralization reaction

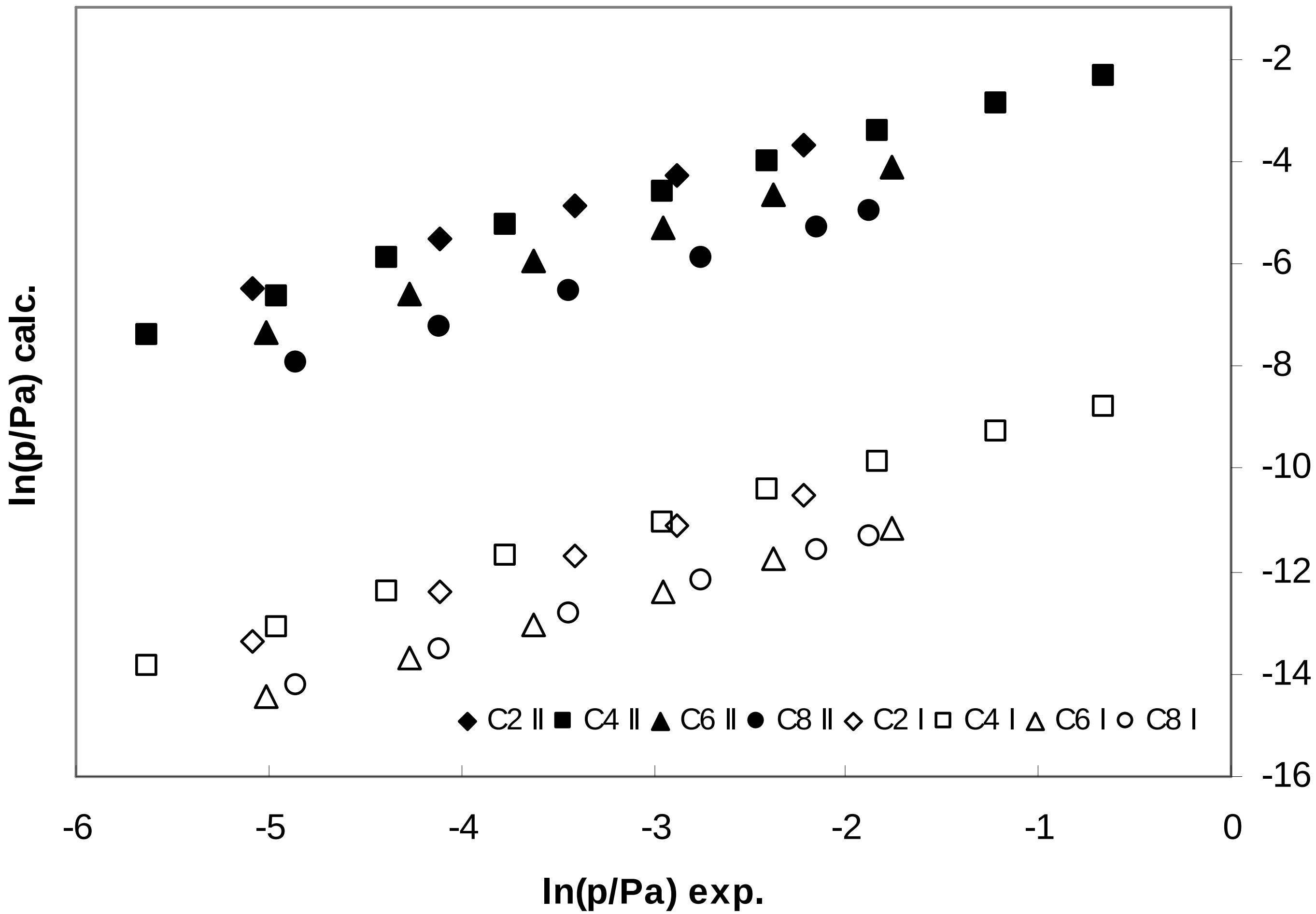


Calculation of the Vapor Pressure (Approach II)

- Do a COSMO-RS standard vapor pressure prediction for the ion pair



Vapor Pressure Predictions



slopes: ~1

max deviations:

I (comb. approach):
9.5 ln (4.1 log) units

II (ion pair only):
~3 ln (1.3 log) units

Exp. data: Dz. H. Zaitsau, G. J. Kabo, A. A. Strechan, Y. U. Paulechka, A. Tschersich, S. P. Verevkin, and A. Heintz, *J. Phys. Chem. A*, 2006, **110**, 7303-7306

Enthalpies of Vaporization [kJ/mol] of [$C_x$mim][NTf_2]

x	<T> /[K]	I comb. approach	II ion pair only	<T> /[K]	exp.
2	464.1	119.5	116.9	463.0	118.8±1.3
4	477.6	120.1	118.9	477.6	118.3±1.7
6	469.7	125.2	123.7	461.8	123.4±0.8
8	478.5	128.4	130.1	475.2	132.3±0.8

Exp. data: Dz. H. Zaitsau, G. J. Kabo, A. A. Strechan, Y. U. Paulechka, A. Tschersich, S. P. Verevkin, and A. Heintz, *J. Phys. Chem. A*, 2006, **110**, 7303-7306

Enthalpies of Vaporization [kJ/mol] at 298 K

IL	calc	exp.
$[C_2mim][EtSO4]$	164.6	164±4[a]
$[C_4mim][dca]$	159.3	157±1.1[b]

dca: dicyanamide

[a] J. P. Armstrong, C. Hurst, R. G. Jones, P. Licence, K. R. J. Lovelock, C. J. Satterley and I. J. Villa-Garcia, *Phys. Chem. Chem. Phys.*, 2007,**9** ,982-990.
[b] V. N. Emel'yanenko, S. P. Verevkin, and A. Heintz, *J. Am. Chem. Soc.*, 2007, *129*, 3930-3937.

Summary

- Activity Coefficients of solutes in Ils can be predicted for finite and infinte dilution
- LLEs with ILs can be predicted
- The vapor pressures of [$C_x$mim][NTf_2] are underestimated whereas the Enthalpie of vaporization is in very good agreement with the experimental value.

Acknowledgements

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- COSMO*logic* team
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