SCM
Software for Chemistry & Materials

COSMO-RS fluid thermodynamics

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Outline

Methods to describe liquids

COSMO-RS

- ADF COSMO result files
- σ-profiles
- interaction energy
- chemical potential

COSMO-SAC 2013-ADF

Binary mixture examples

Properties

Methods to describe liquids

Molecular dynamics, Monte Carlo simulations

- MM or DFT potential energy surface
- expensive, often not feasible

COSMO-RS, COSMO-SAC

- molecule is represented by charge density on DFT COSMO surface
- statistically thermodynamics of (fitted) interacting surfaces
- general applicable

UNIFAC, UNIQUAC

- molecule is sum of functional groups
- properties functional group fitted to experiment
- can fail for complex molecules

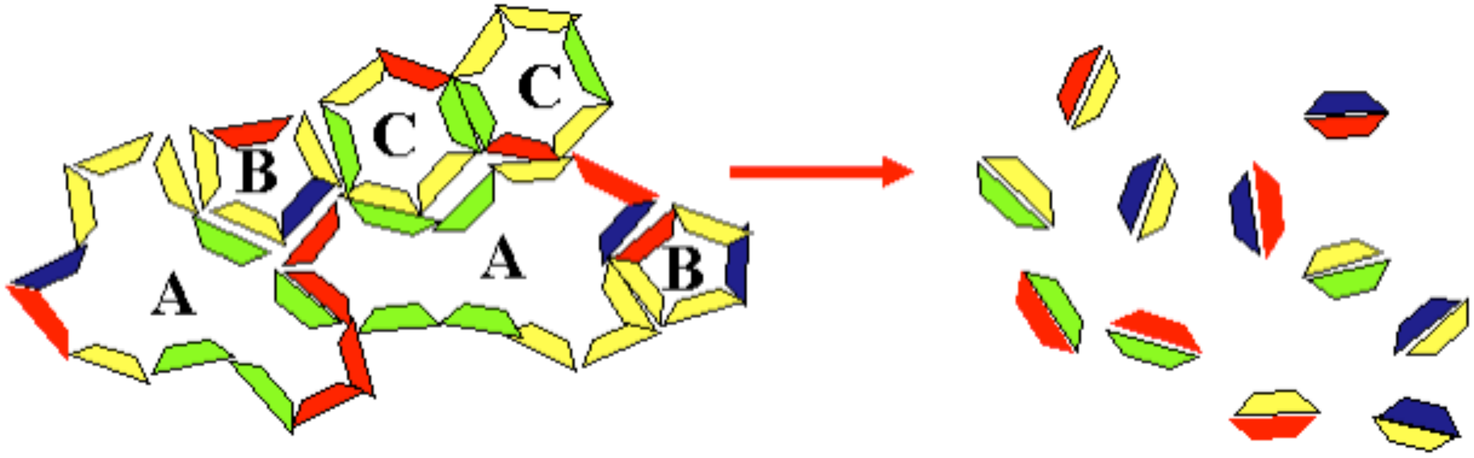
COSMO-RS

COnductor-like **S**creening **MO**del for **R**ealistic **S**olvents

A. Klamt J. Phys. Chem 99 (1995) 2244, A. Klamt et al. J. Phys. Chem. A 102 (1998) 5074

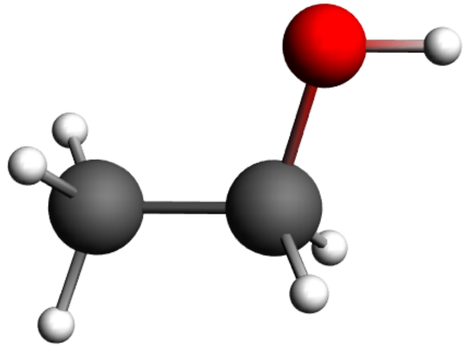
C.C. Pye, T. Ziegler, E. van Lenthe, J.N. Louwen, Can. J. Chem. 87 (2009), 790

- thermodynamic properties, equilibrium
- calculates chemical potential
  - σ-profile: charge density on COSMO surface
  - electrostatic interactions + hydrogen bond
  - effective contact area
  - random mixture approximation
  - Boltzmann distribution
- COSMO-RS parameters
  - fitted to experiment

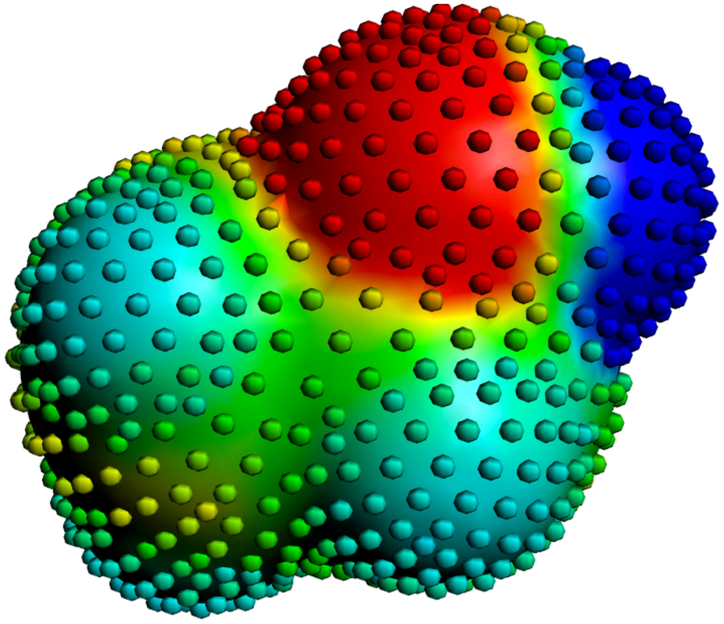


COSMO

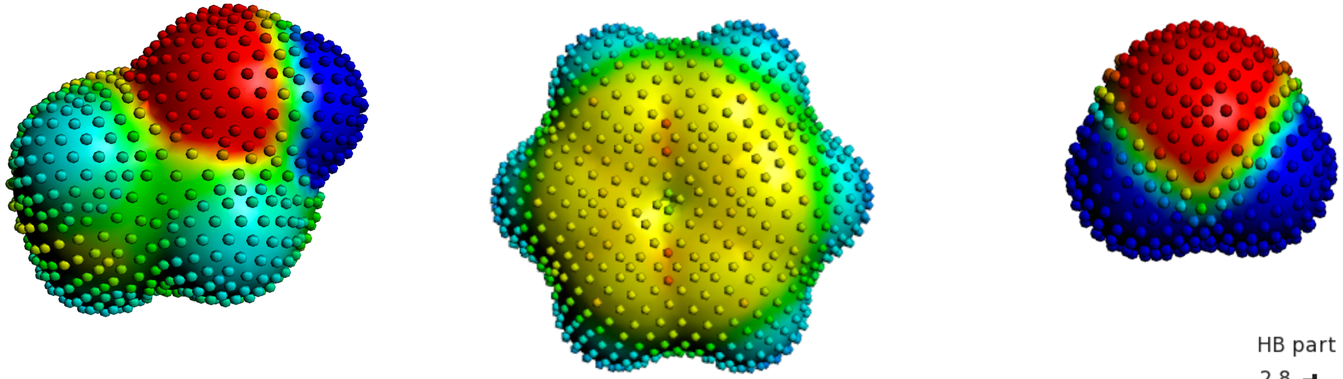
COnductor-like **S**creening **MO**del
solute embedded in molecule-shape cavity
    element specific COSMO-radii
dielectric continuum outside cavity
    for COSMO-RS: ideal conductor ε = ∞
COSMO volume predicts molar density
ADF DFT molecular calculation (BP86 TZP)

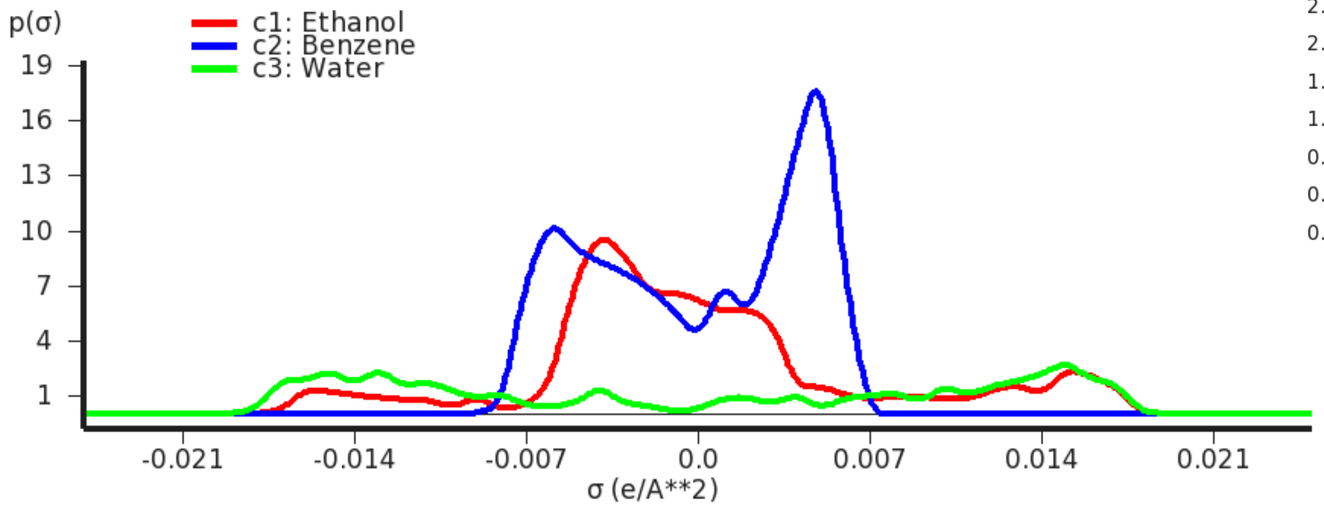


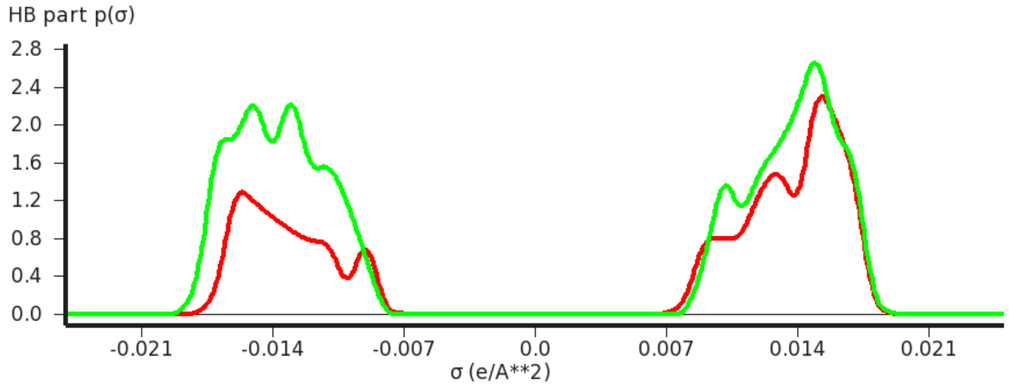
Ethanol



σ-profiles




p(σ)
c1: Ethanol
c2: Benzene
c3: Water
19
16
13
10
7
4
1
-0.021
-0.014
-0.007
0.0
0.007
0.014
0.021
σ (e/A**2)


HB part p(σ)
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0.0
-0.021
-0.014
-0.007
0.0
0.007
0.014
0.021
σ (e/A**2)

Interaction energy

pair-wise interactions, random mixture approximation

misfit energy repulsive

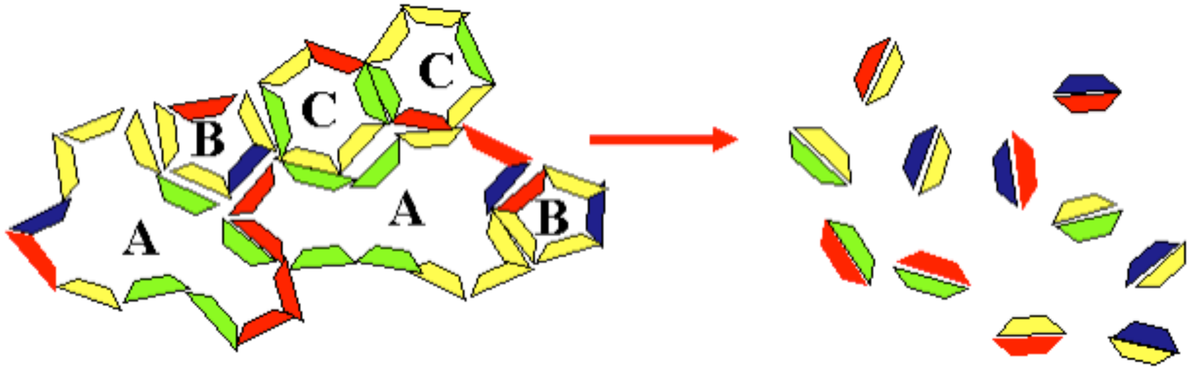
$$E(\sigma,\sigma') = c\,(\sigma+\sigma')^2$$

hydrogen bonding attractive

$$E_{HB}(\sigma_{HB},\sigma_{HB}')$$

σ-potential

$$\mu_s(\sigma) = -kT \ln \Sigma_{\sigma'} p_s(\sigma') \exp\{[-E_{int}(\sigma,\sigma')+ \mu_s(\sigma')]/kT\}$$



Chemical potential

liquid chemical potential

$$\mu^i = \Sigma_\sigma\, p^i(\sigma)\, \mu_s(\sigma) + \text{combinatorial terms}$$

gas chemical potential

$$\mu_{gas}{}^i = E_{gas}{}^i - E_{cosmo}{}^i + \text{dispersion terms}$$

solid chemical potential

$$\mu_{solid}{}^i - \mu^i = \Delta G_{fus}$$

activity coefficients shows deviations from ideal

$$\gamma_s{}^i = \exp\{(\mu_s{}^i - \mu_{pure}{}^i)/kT\}$$

vapor pressure pure compound

$$p = \exp\{-(\mu_{gas}{}^x - \mu_{pure}{}^x)/kT\}$$

COSMO-RS in ADF

COSMO-RS in ADF

C.C. Pye, T. Ziegler, E. van Lenthe, J.N. Louwen, Can. J. Chem. 87 (2009), 790

216 molecules, 642 experimental data	accuracy (rms)
log vapor pressures (bar)	0.24 log units
hydratation energies	0.37 kcal/mol
partition coefficients	0.35 log units

(octanol/water,benzene/water, hexane/water, diethyl ether/water)

COSMO-SAC 2013-ADF in ADF

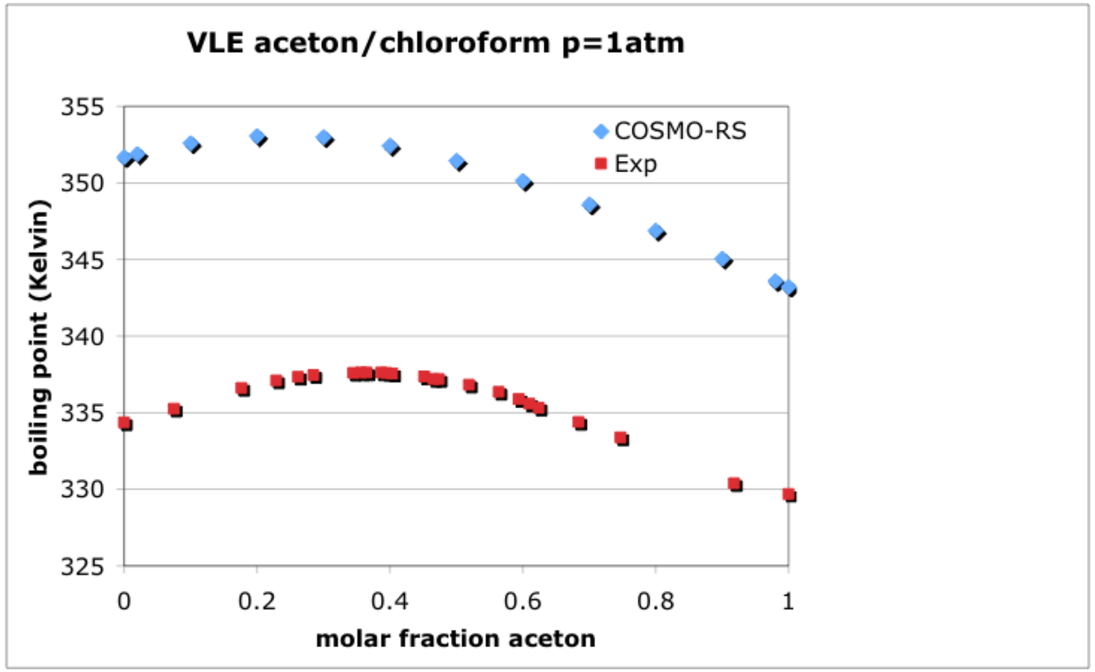
R. Xiong, S.I. Sandler, R.I. Burnett, Ind. Eng. Chem. Res. 53 (2014) 8265

SAC = segment activity coefficients

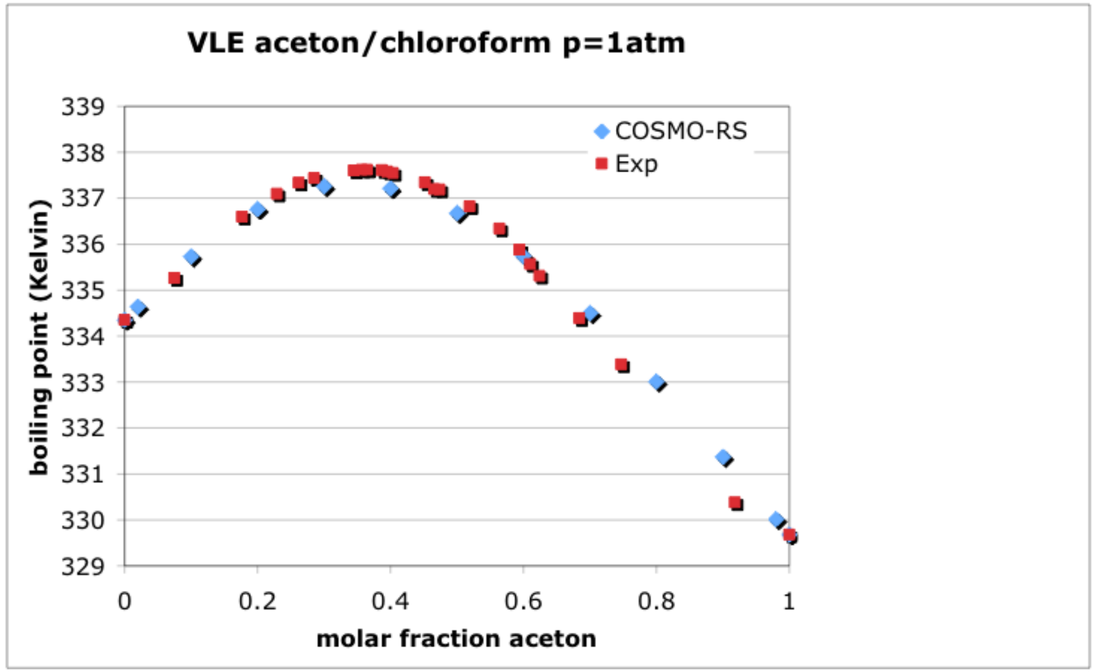
optimized parameters for ADF

dispersion contribution in the mixture interaction

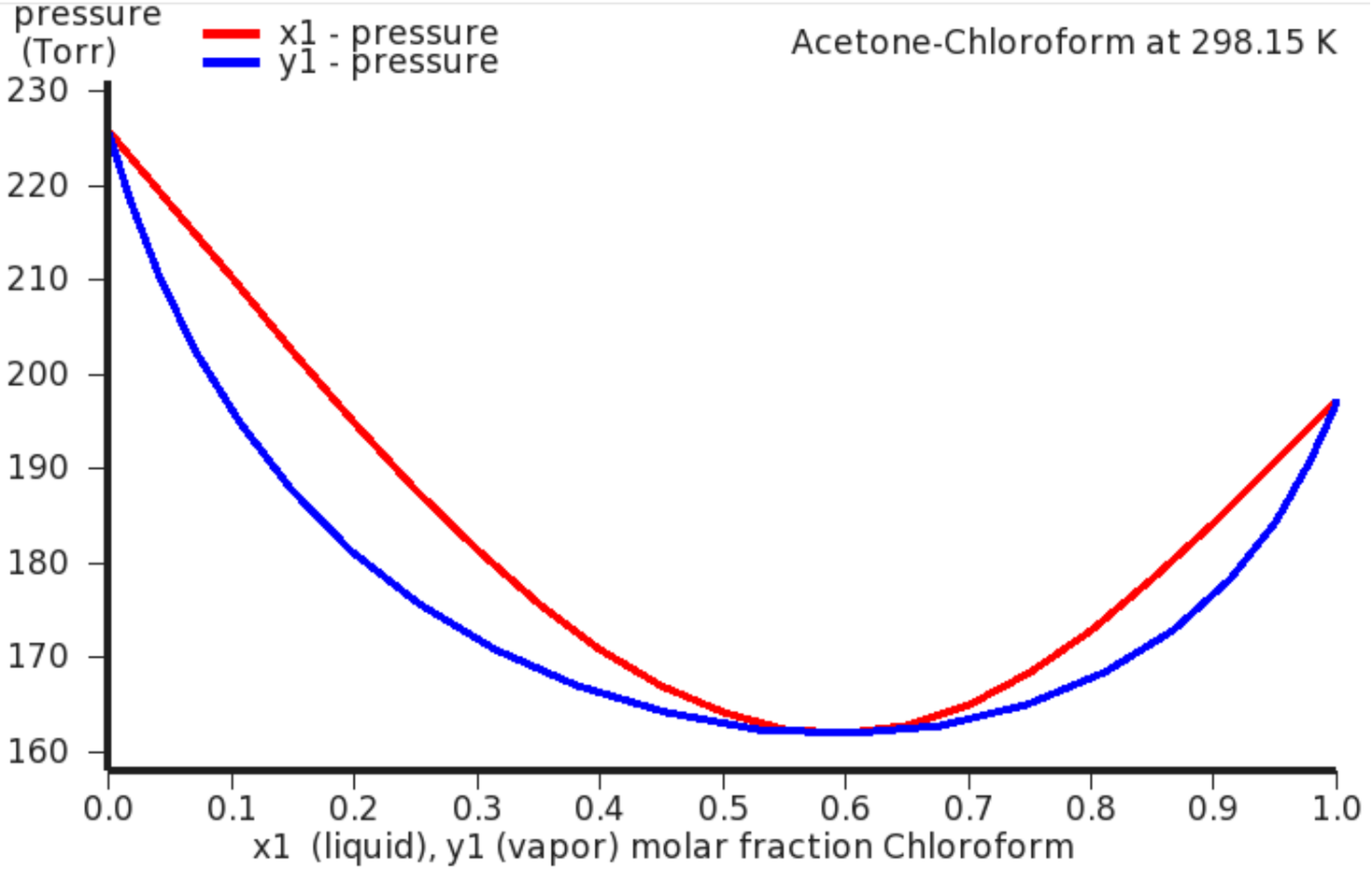
Aceton Chloroform VLE

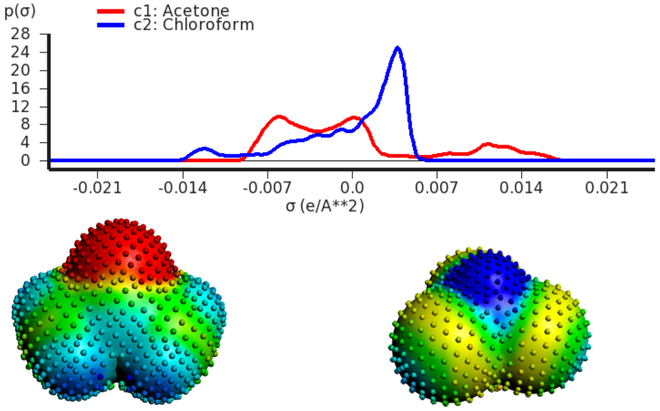


Use of experimental pure compound data



Acetone Chloroform azeotrope





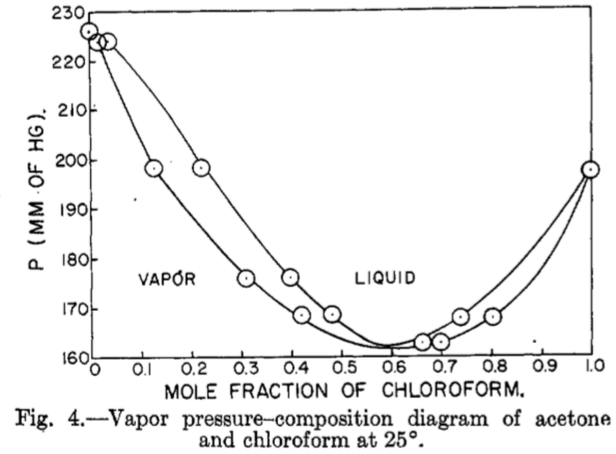
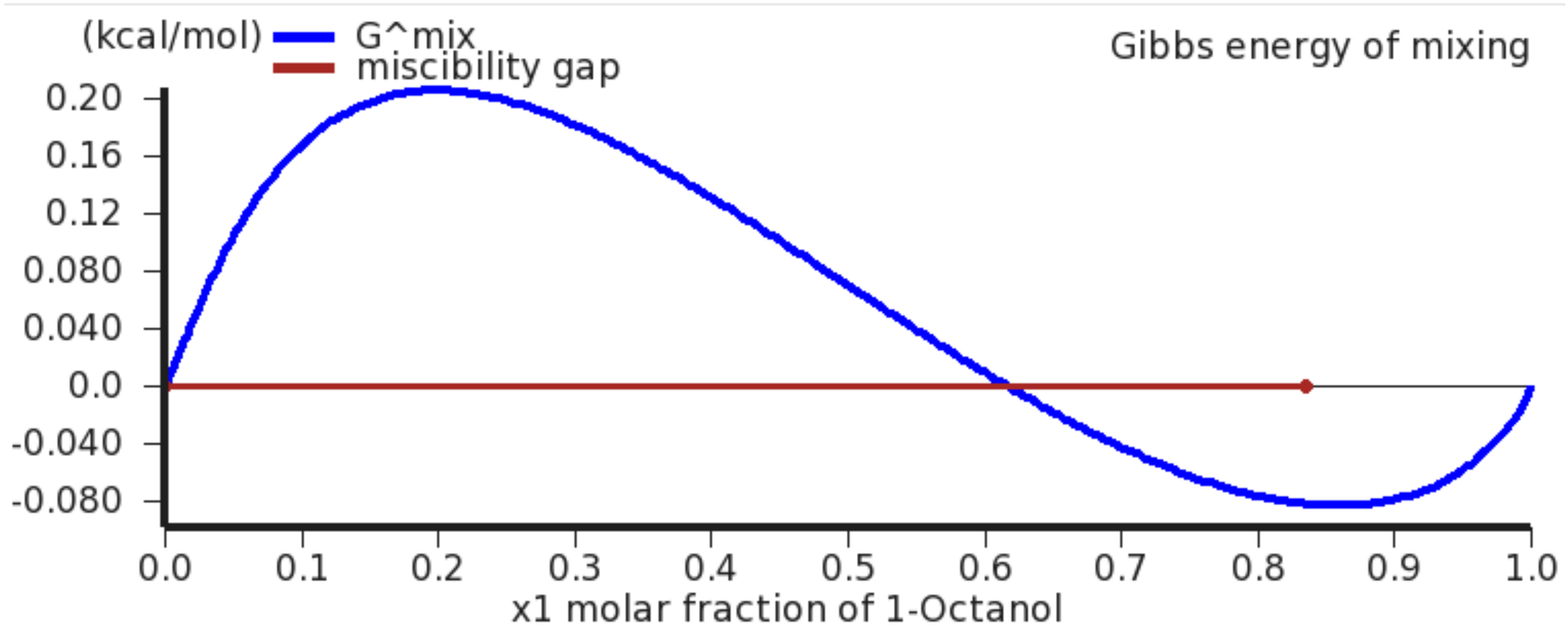
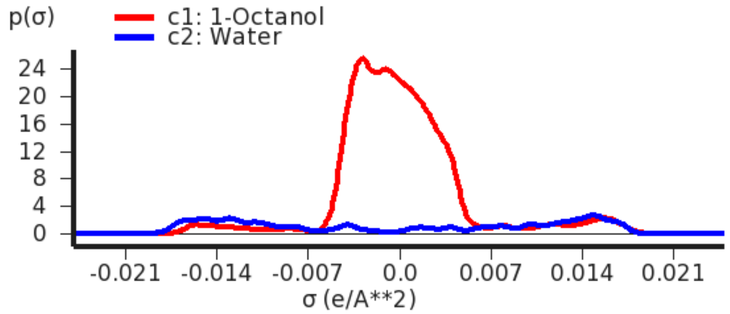


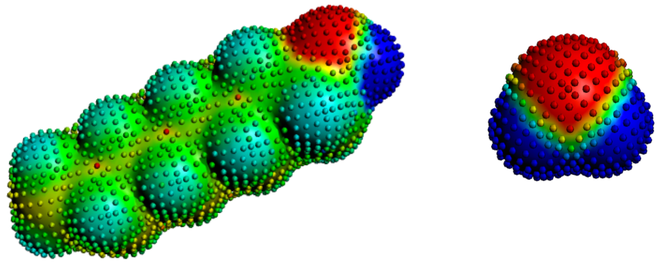
Fig. 4.—Vapor pressure–composition diagram of acetone and chloroform at 25°.

Mueller, Kearns, J. Phys. Chem.,1958, 62 1441

1-Octanol Water miscibility gap







Properties

Solubility gas, liquid, or solid in solvent

for solids experimental melting point + ΔH_{fus} needed

Partition coefficients

K_{OW} relative solubilities in 1-Octanol and Water

pKa values

activity coefficients, solvation free energies, Henry's law constants

vapor pressures, boiling points

vapor-liquid diagrams binary and ternary mixtures (VLE/LLE)

excess energies, azeotropes, miscibility gaps

composition lines, flash points

2016

ionic liquid database

Dr. Zhigang

command-line scripts

pure compound COSMO-SAC ADF-2013