Phase-Equilibrium Predictions for Hydrogen-Bonding Systems from a New Expression for COSMO Solvation Models

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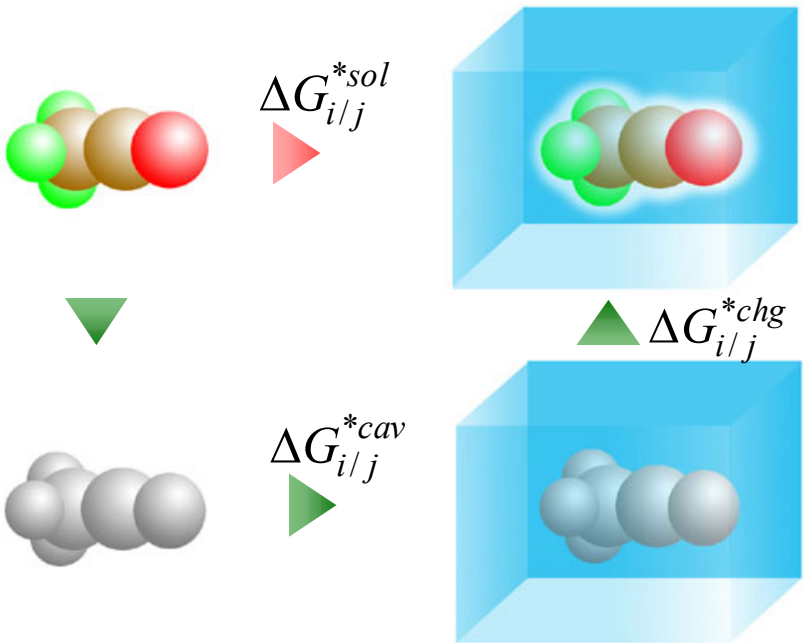
AIChE Annual Meeting
Indianapolis, IN, 3-8 November 2002

Goals

Evaluation and improvement of the COSMO-SAC model for the prediction of activity coefficients of highly non-ideal systems:

- How does it compare with UNIFAC?
- Can it be improved by a new expression for the hydrogen-bonding exchange energy?
- Is it ready for broad industrial application?
- If not, where is improvement needed?

Phase Behavior from Solvation



equilibrium criteria

$T^{I} = T^{II}$

$P^{I} = P^{II}$

$f_i^{I} = f_i^{II}$

$f_i = x_i \gamma_i f_i^0$

$f_i^0 \cong P_i^{vap}$

- Solvation Thermodynamics

$$\ln \gamma_{1/2} = \frac{\Delta G_{1/2}^{*sol} - \Delta G_{1/1}^{*sol}}{RT} + \ln \frac{c_2}{c_1^0}$$

$$\ln P_1^{vap} = \frac{\Delta G_{1/1}^{*sol}}{RT} + \ln c_1^0 RT$$

$\Delta G_{i/j}^{*sol}$: solvation free energy

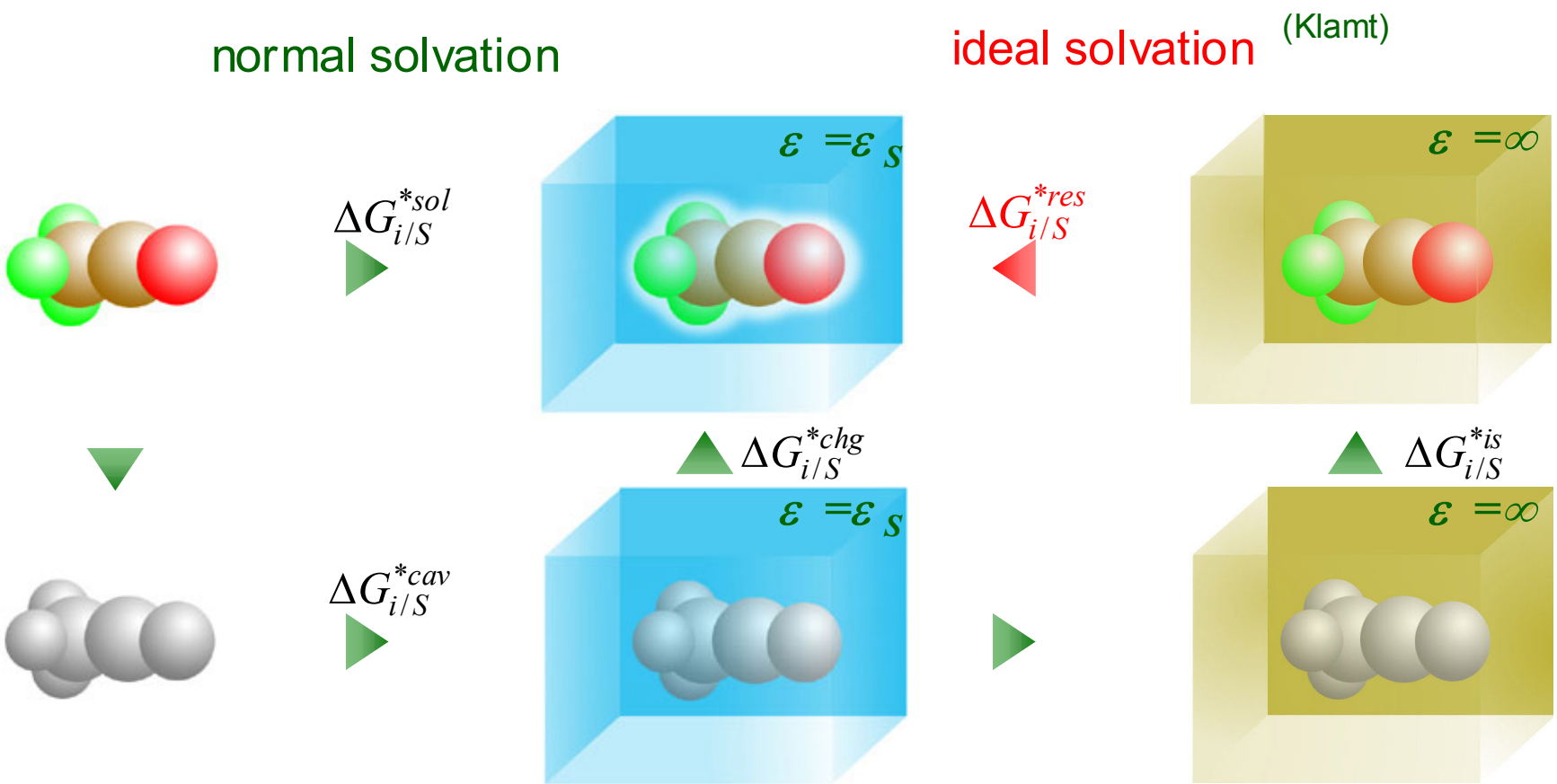
$\Delta G_{i/j}^{*cav}$: cavity formation free energy

$\Delta G_{i/j}^{*chg}$: charging free energy

i/j : solute *i* in solvent *j*

c : total molar concentration

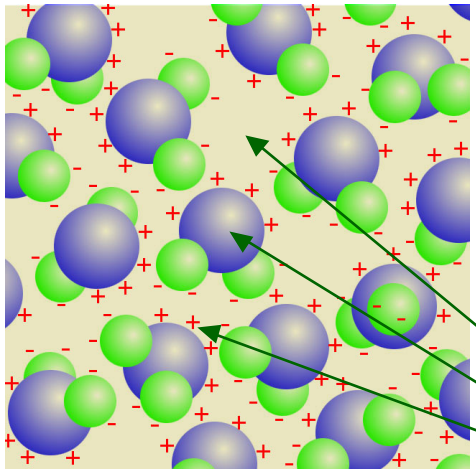
Solvation free Energy from COSMO models



$$\Delta G^{*sol}_{i/S} = \Delta G^{*res}_{i/S} + \Delta G^{*is}_{i/S} + \Delta G^{*cav}_{i/S}$$

Phase Behavior from COSMO-RS Models

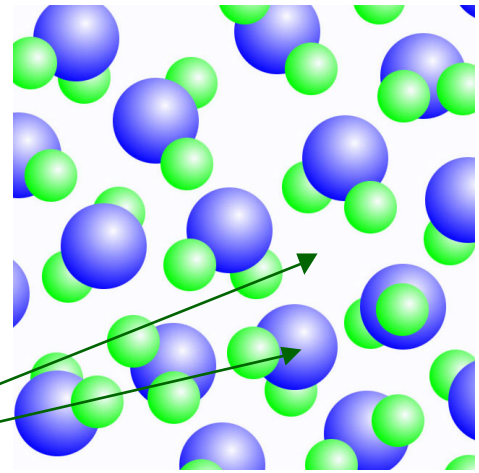
Ideal Solvation



conductor
water molecule
screening charge

$$\Delta G_{i/S}^{*res}$$

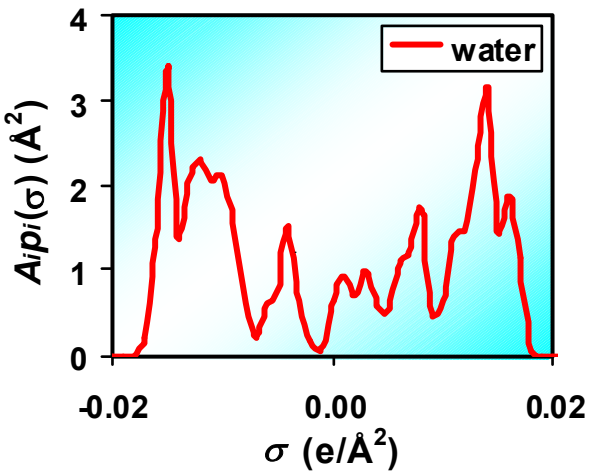
Real Solution



real solvent
water molecule

consider each molecule as a collection of surface segments

σ - profile



remove screening charges on segments

Activity Coefficients

$$\ln \Gamma_s(\sigma_m) = -\ln\left\{\sum_{\sigma_n} p_j(\sigma_n)\Gamma_S(\sigma_n)\exp\left[\frac{-\Delta W(\sigma_m,\sigma_n)}{kT}\right]\right\}$$ – Segment γ

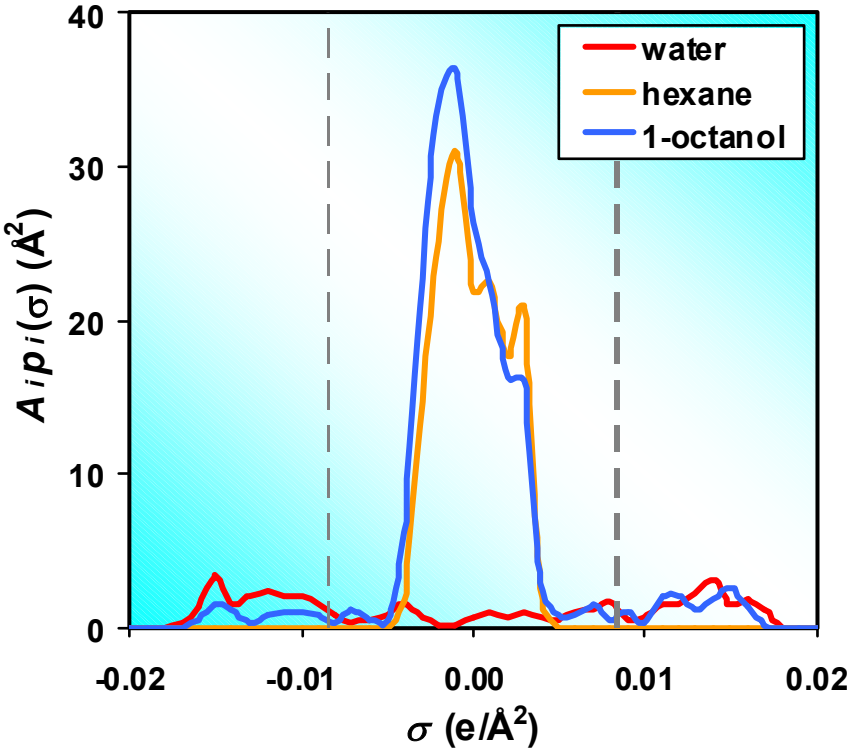
$$\Delta W(\sigma_m,\sigma_n) = \frac{\alpha'}{2}(\sigma_m+\sigma_n)^2 + \Delta W^{HB}(\sigma_m,\sigma_n)$$ – Exchange energy

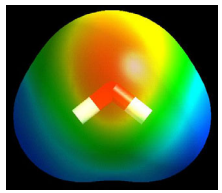
$$\ln \gamma_i = \frac{A_i}{a_{\text{eff}}}\sum_{\sigma_m} p_i(\sigma_m)\left[\ln \Gamma_S(\sigma_m) - \ln \Gamma_i(\sigma_m)\right] + \ln \gamma_i^{SG}$$ – Molecule γ

γ_i	Activity coefficient of component *i*
γ_i^{SG}	Staverman-Guggenheim model for combinatorial contribution to γ_i
$\Gamma_S(\sigma_m)$	Segment activity coefficient of segment σ_m in solvent mixture
$\Delta W(\sigma_m, \sigma_n)$	Exchange energy between segments σ_m and σ_n
$\Delta W^{HB}(\sigma_m, \sigma_n)$	Hydrogen-bonding contribution to exchange energy between segments σ_m and σ_n

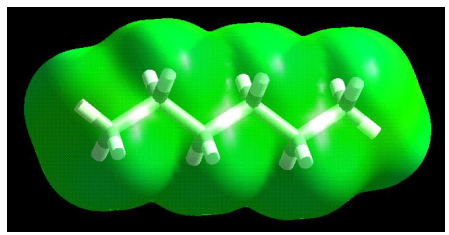
The σ-Profile

- σ-profile

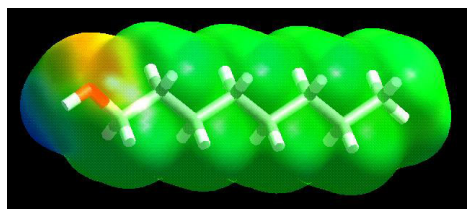




water



hexane

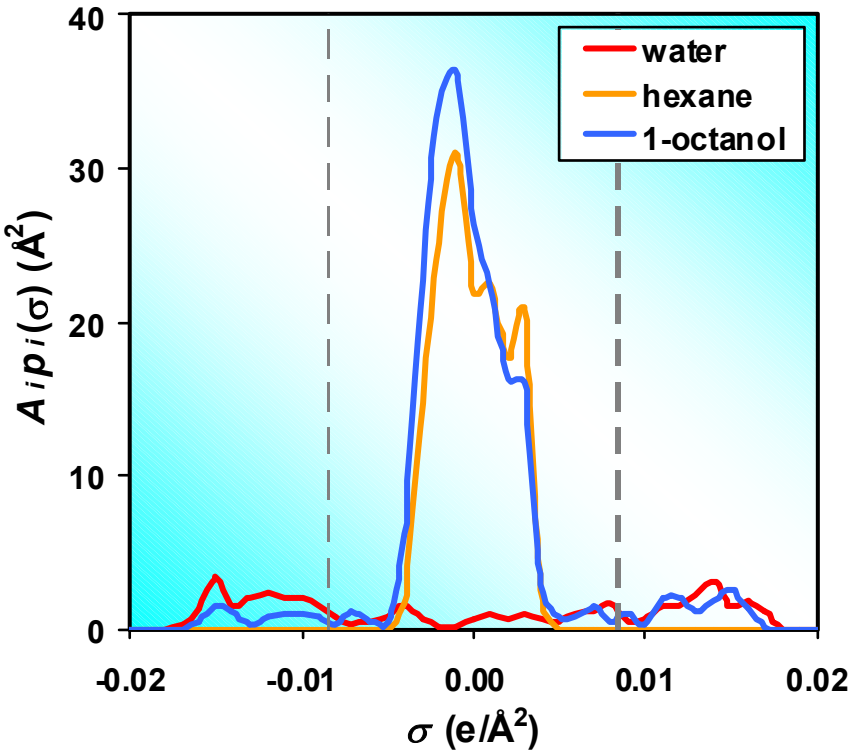


1-octanol

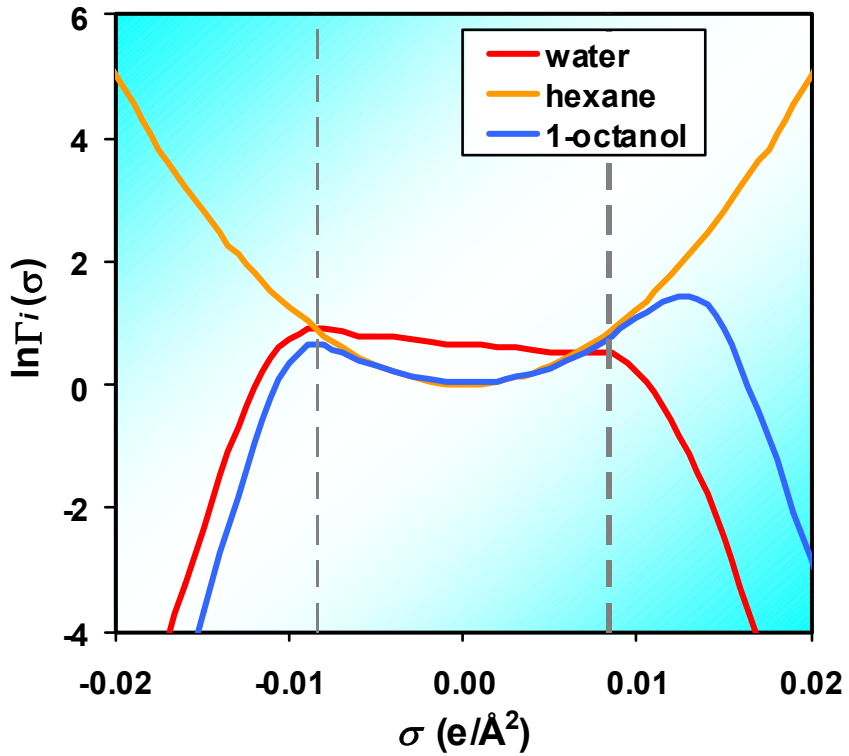
The σ-Profile and Segment Activity Coefficients

$$\ln \Gamma_s(\sigma_m) = -\ln\left\{\sum_{\sigma_n} p_j(\sigma_n)\Gamma_S(\sigma_n)\exp\left[\frac{-\Delta W(\sigma_m,\sigma_n)}{kT}\right]\right\}$$

σ-profile



Segment activity coefficient



Hydrogen-Bonding Exchange Energy

Original Model

$$\Delta W^{HB}(\sigma_m, \sigma_n) = c_{\mathrm{HB}} \max[0, \sigma_{\mathrm{acc}} - \sigma_{\mathrm{hb}}] \min[0, \sigma_{\mathrm{don}} + \sigma_{\mathrm{HB}}]$$

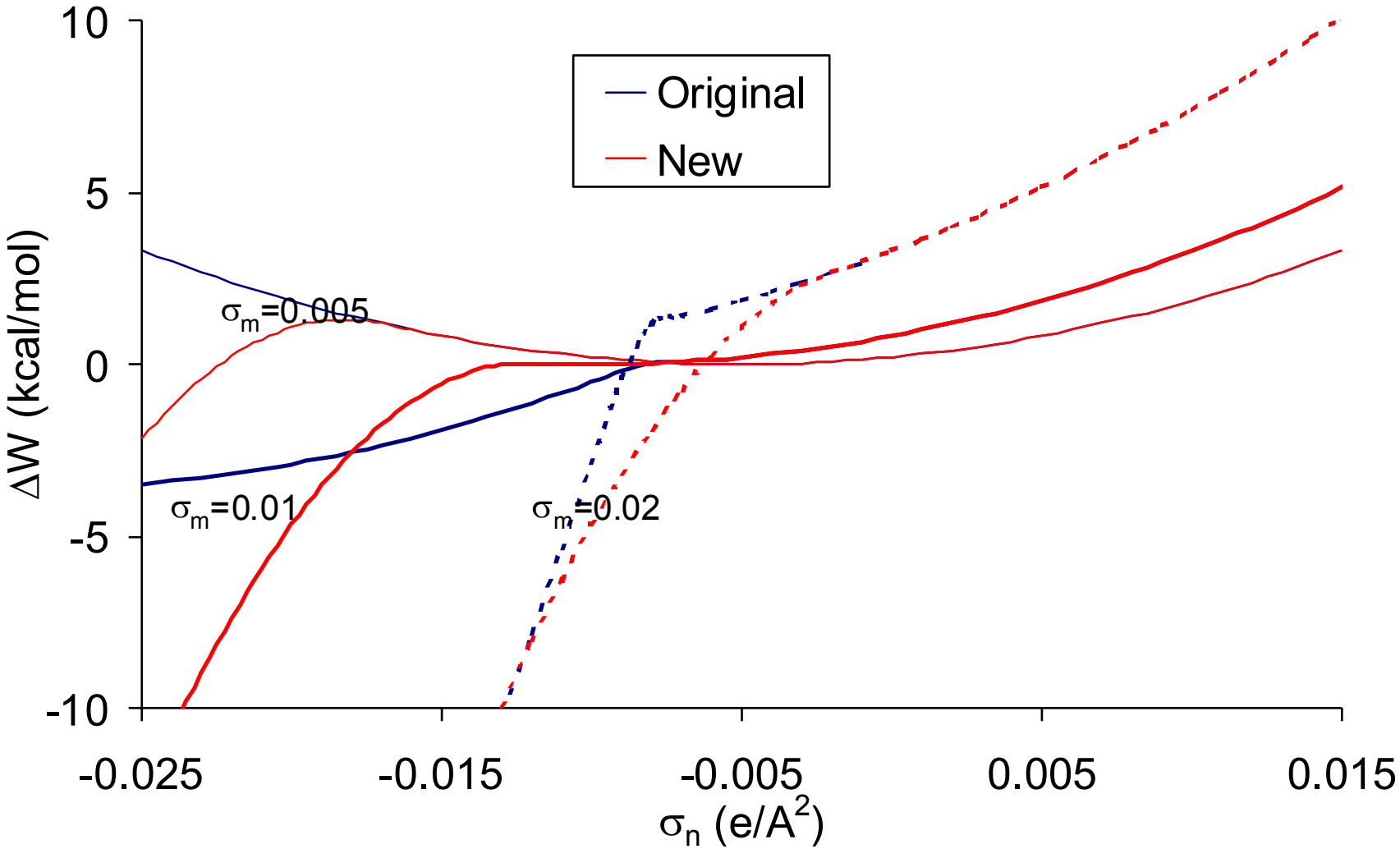
$$\sigma_{acc} = \max(\sigma_m, \sigma_n) \qquad \sigma_{don} = \max(\sigma_m, \sigma_n) \qquad \sigma_{HB} = 0.0084$$

New Model

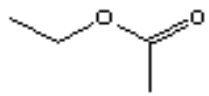
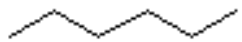
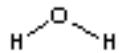
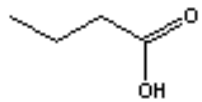
$$\Delta W^{HB}(\sigma_m, \sigma_n) = -c_{HB}^{N} \left\{ \max\left[0, |\sigma_m - \sigma_n| - \sigma_{HB}^{n}\right] \right\}^2$$

$$\sigma_{HB} = 0.022$$

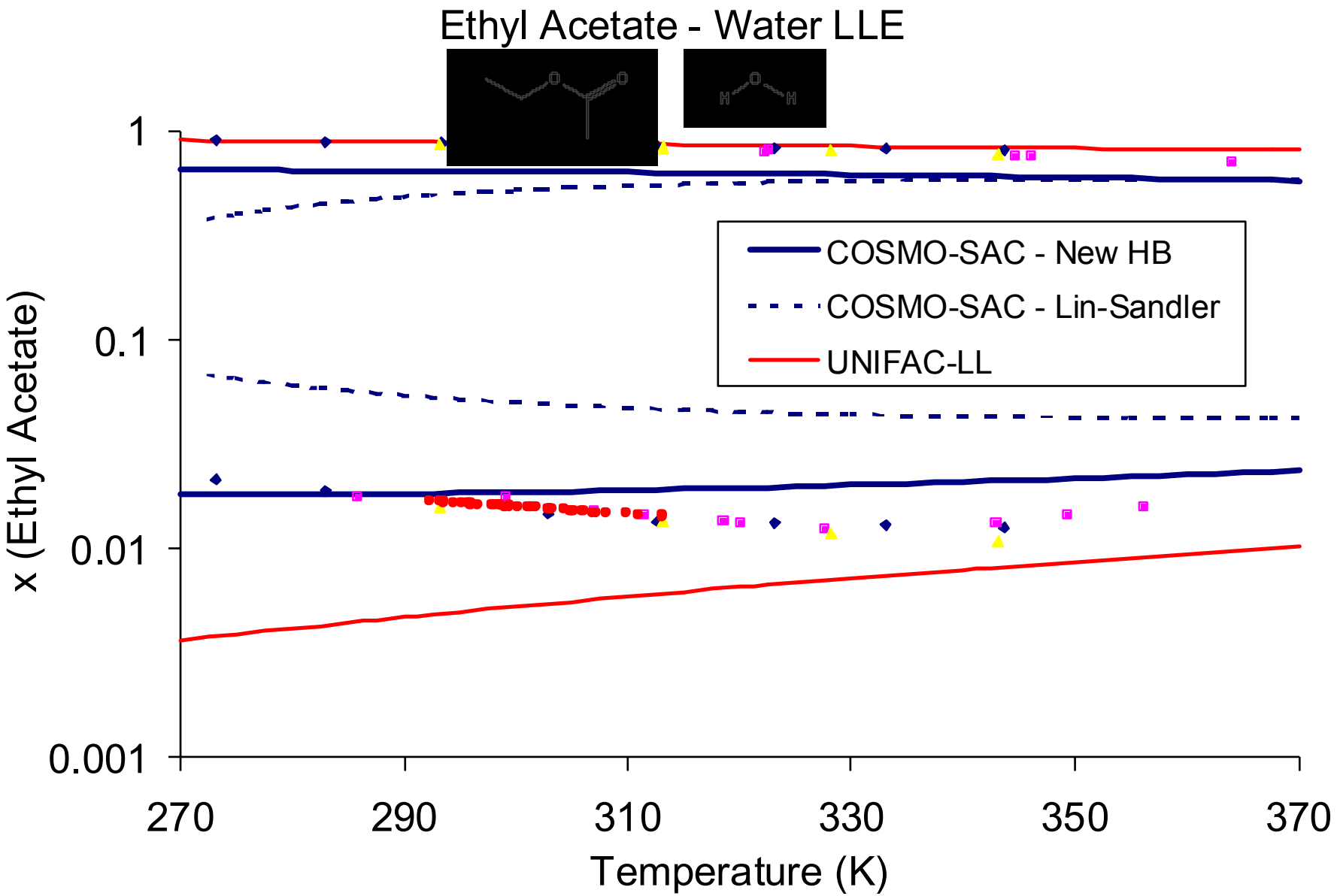
Exchange Energy from Original and New Hydrogen-Bonding Terms



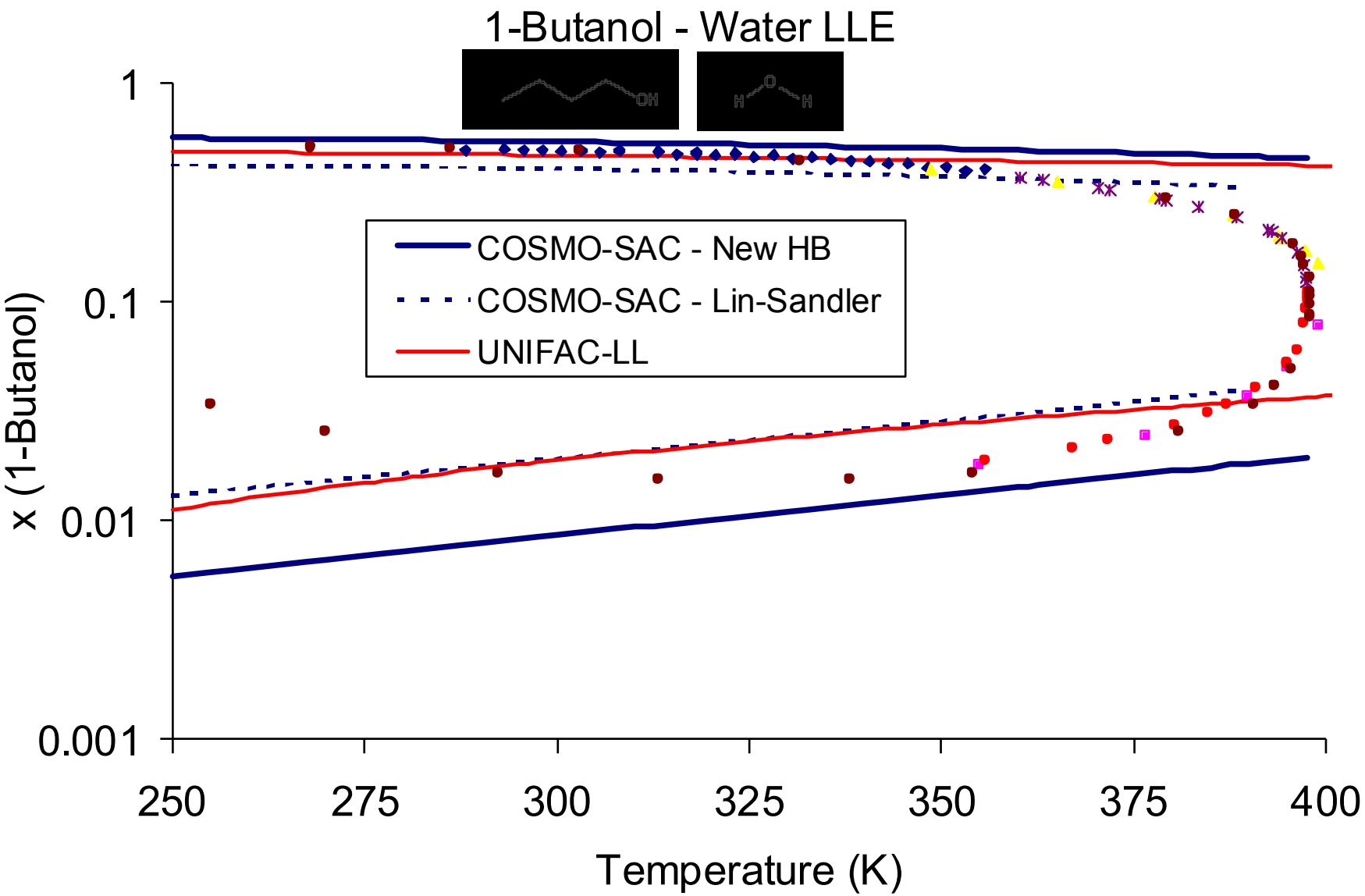
Compounds Studied

Name	Formula	Structure
1. Ethyl Acetate	$C_4H_8O_2$	
2. 1-Butanol	$C_4H_{10}O$	
3. 1,4-Dioxane	$C_4H_8O_2$	
4. n-Hexane	C_6H_{14}	
5. Water	H_2O	
6. Butyric Acid	$C_4H_8O_2$	
7. Butylamine	$C_4H_{11}N$	
8. Butyronitrile	C_4H_7N	

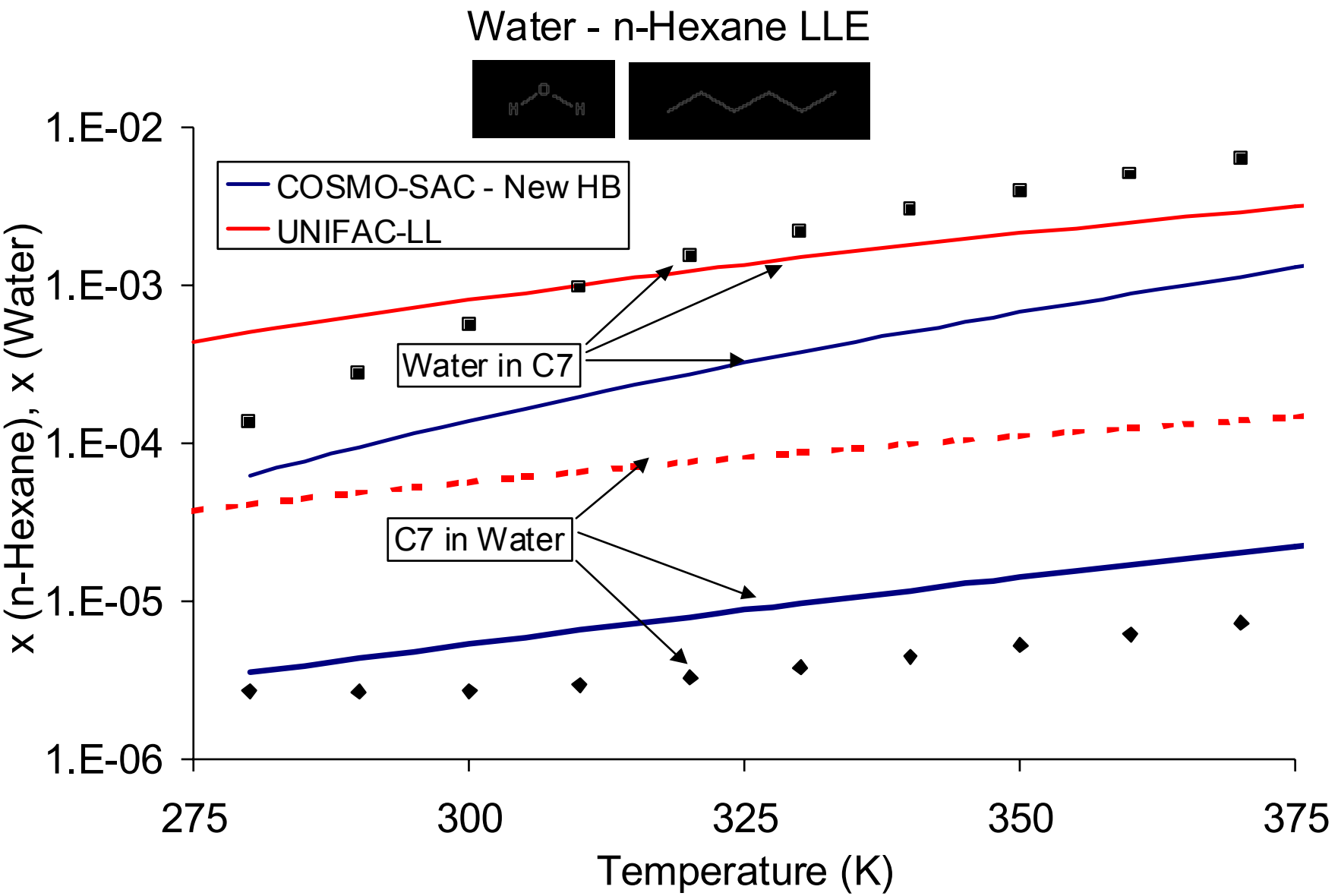
Results – LLE



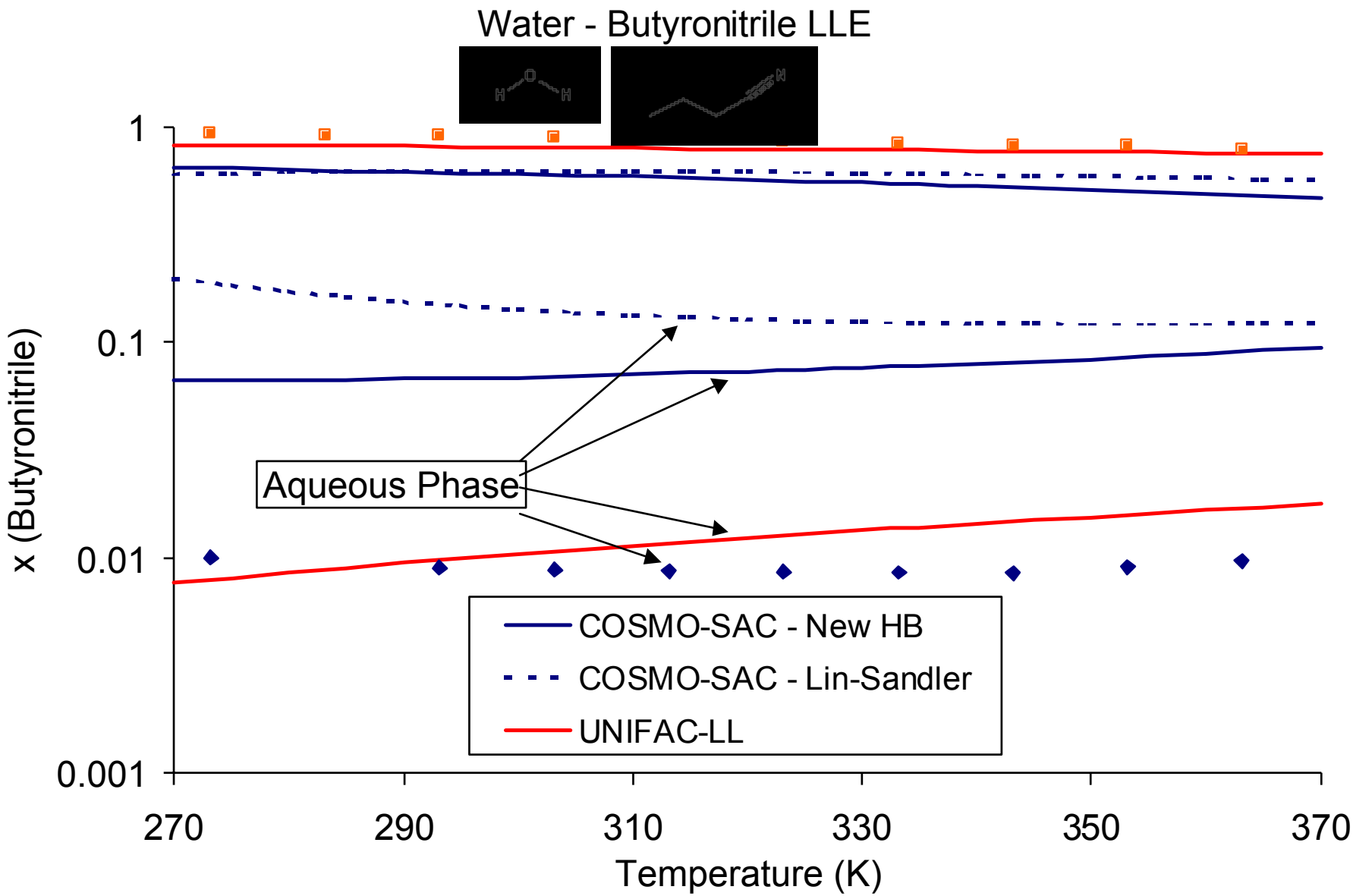
Results – LLE



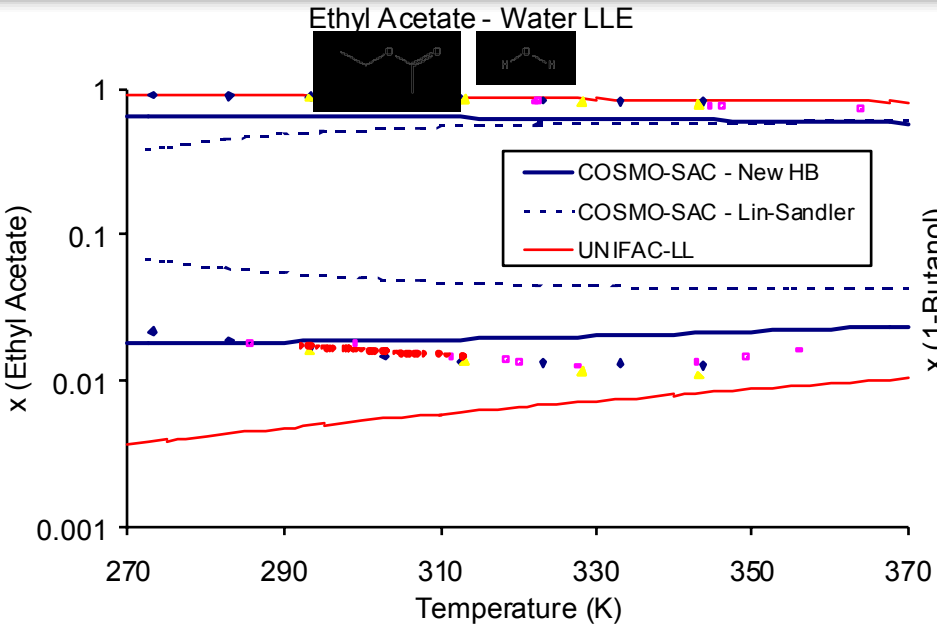
Results – LLE

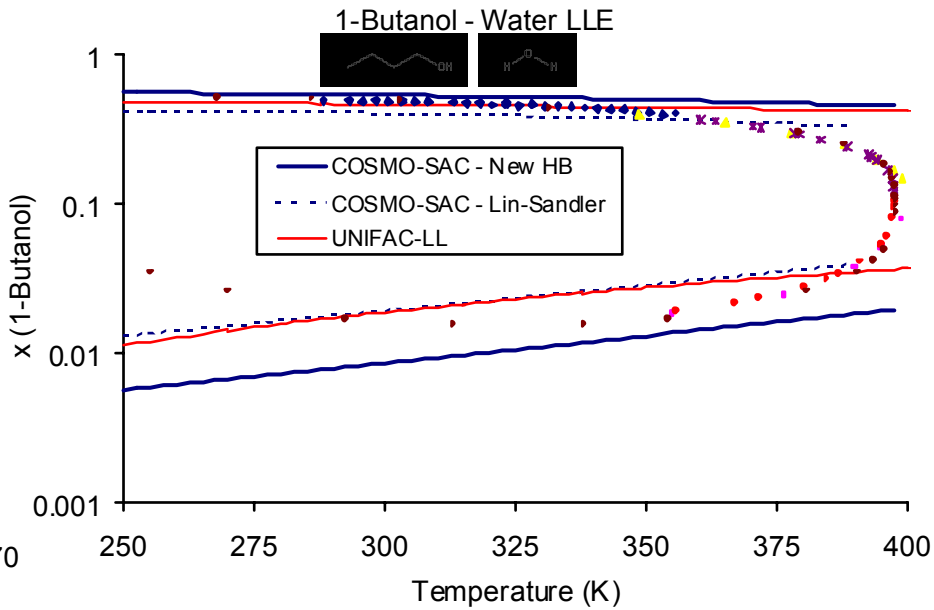


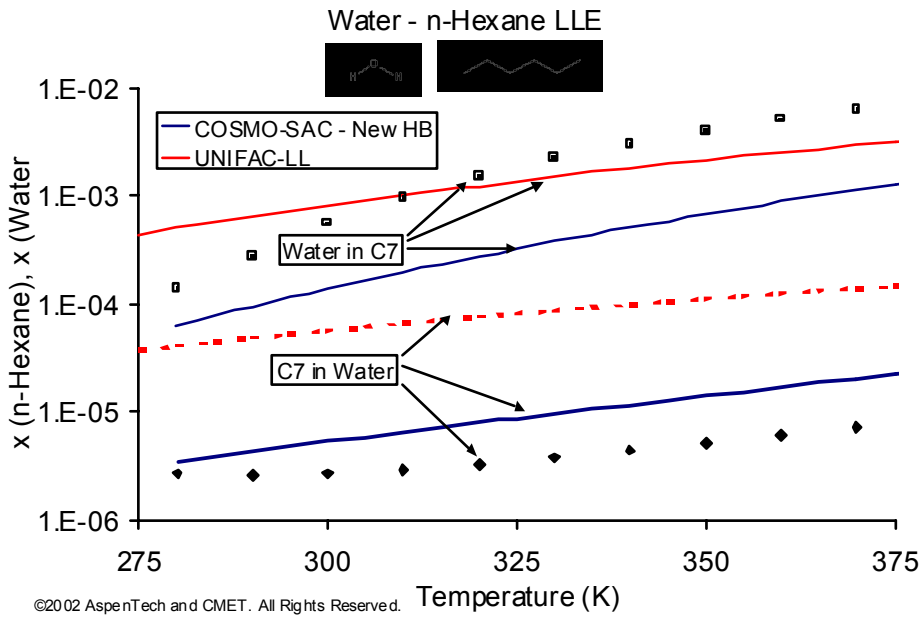
Results – LLE

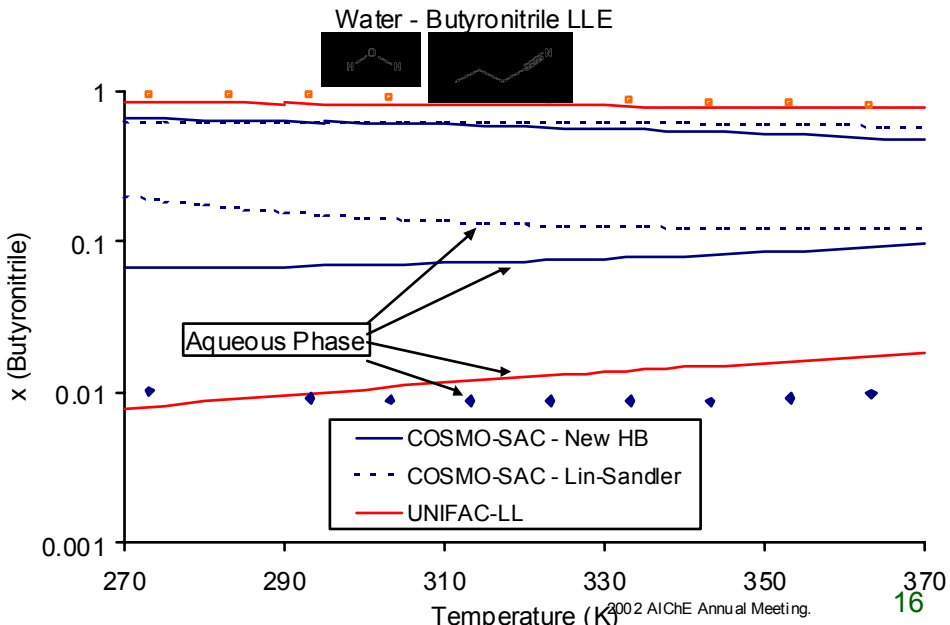


Results – LLE

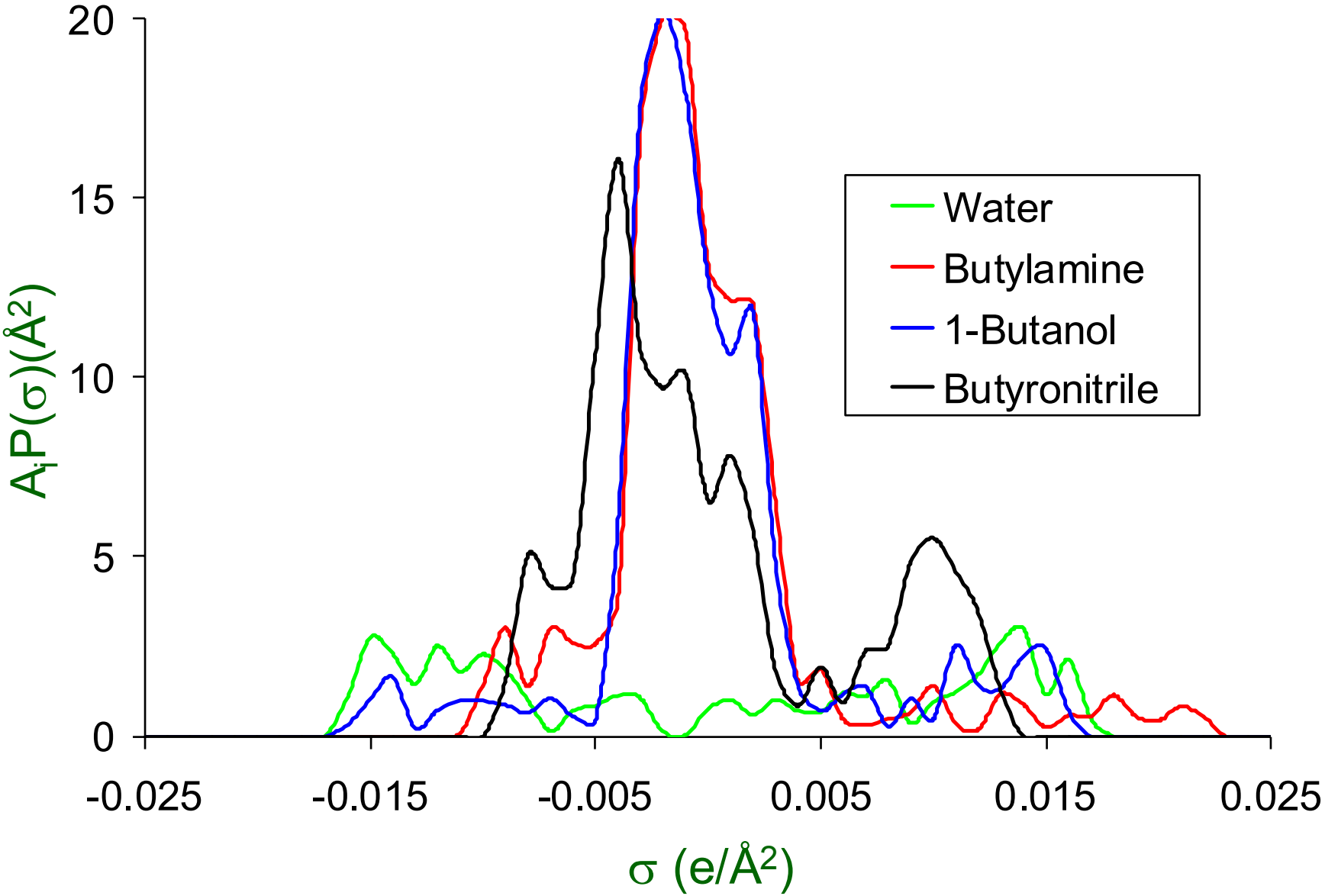




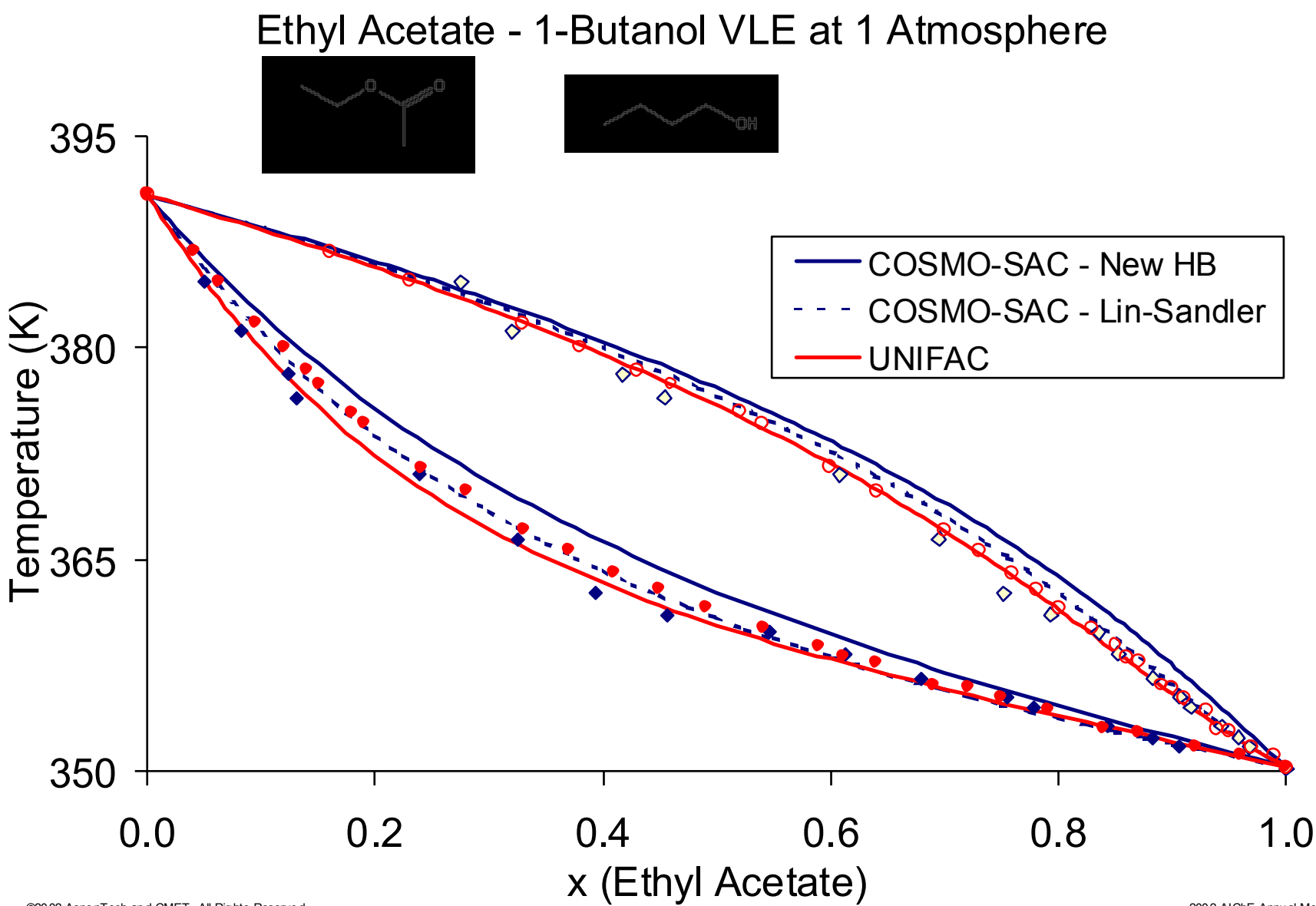




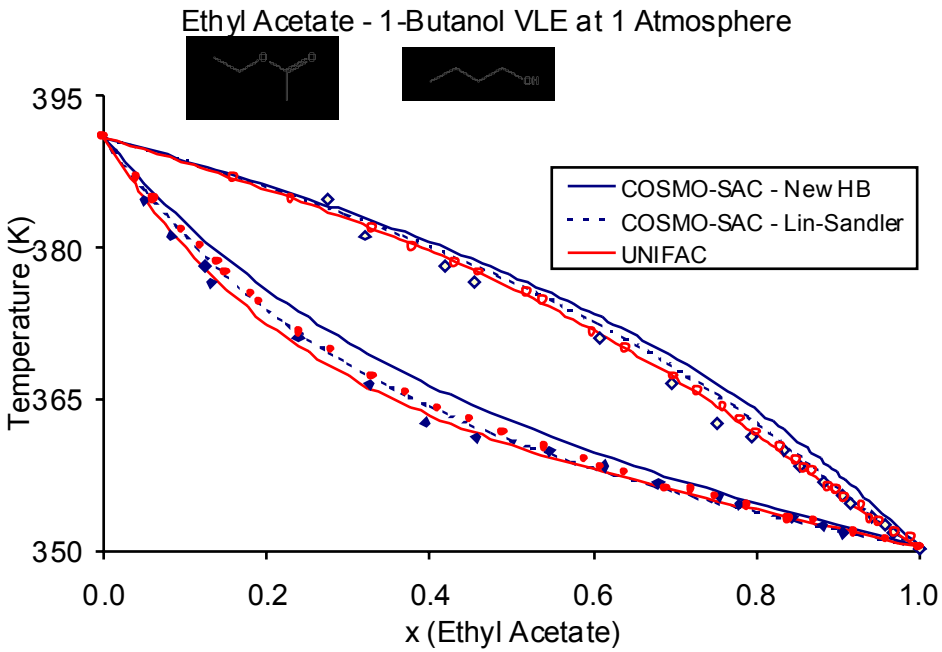
Selected σ–Profiles

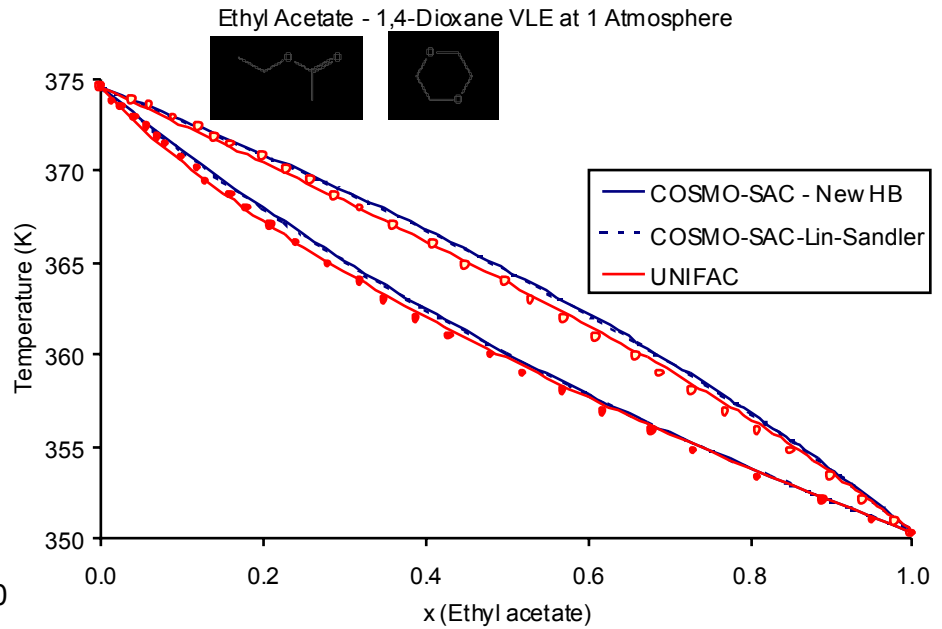


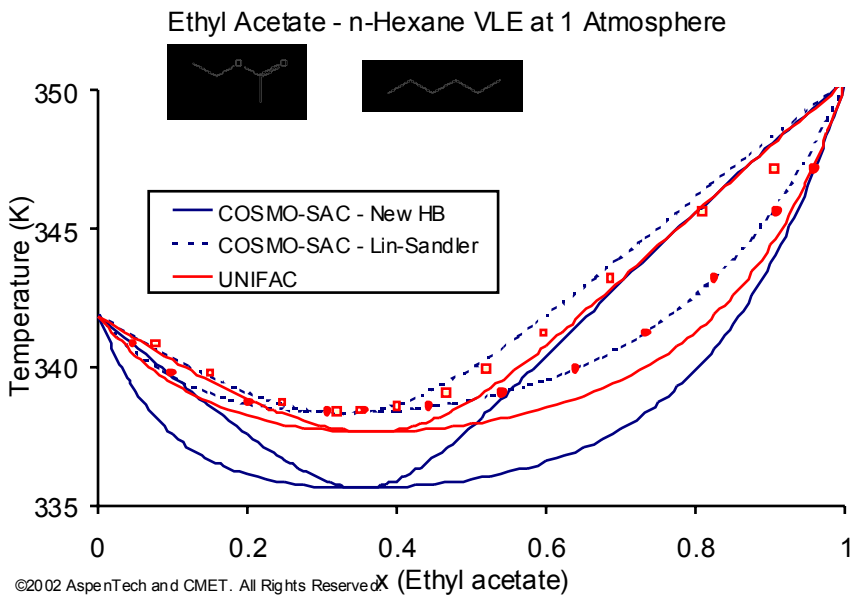
Results – VLE-1

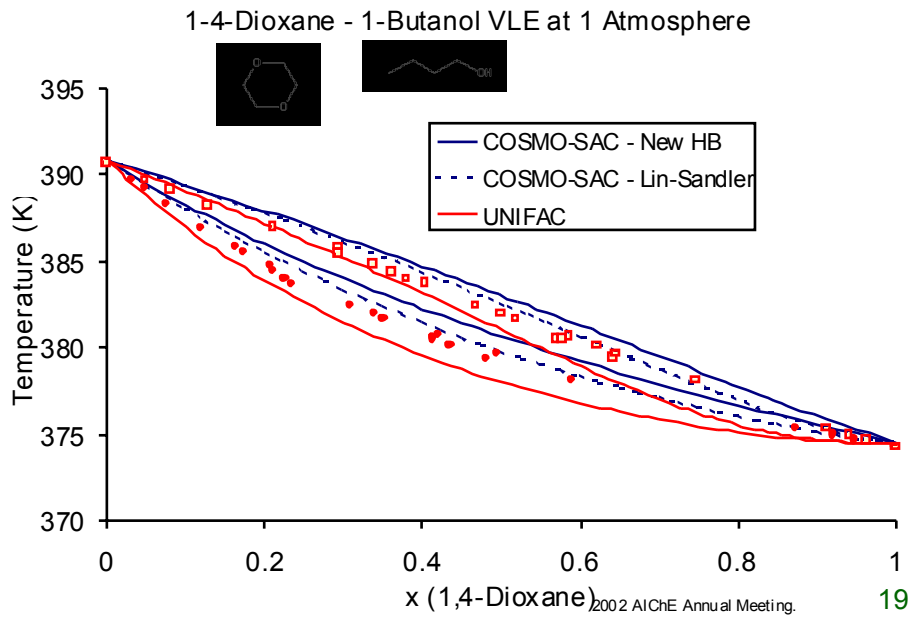


Results – VLE-1

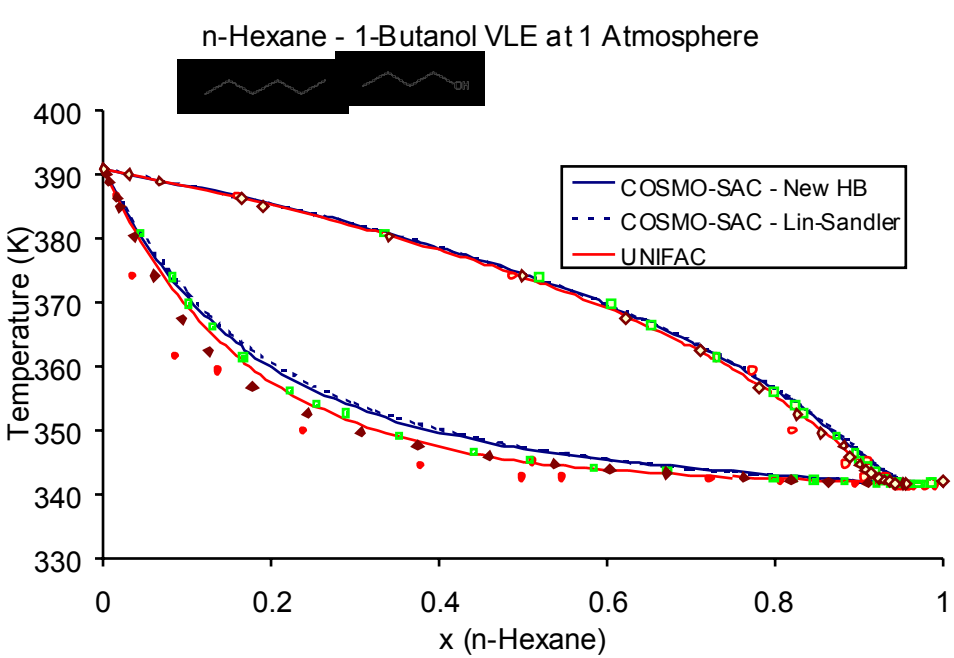


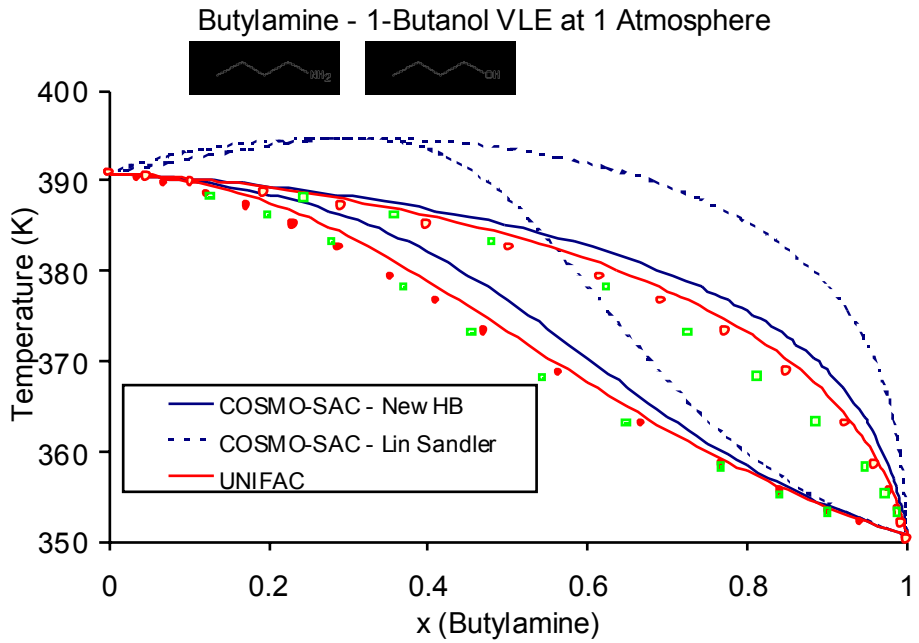


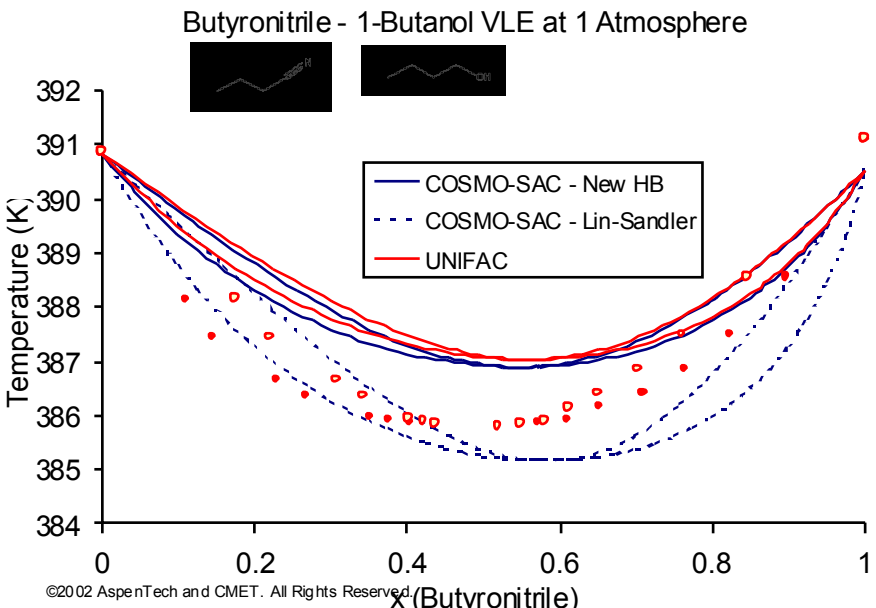


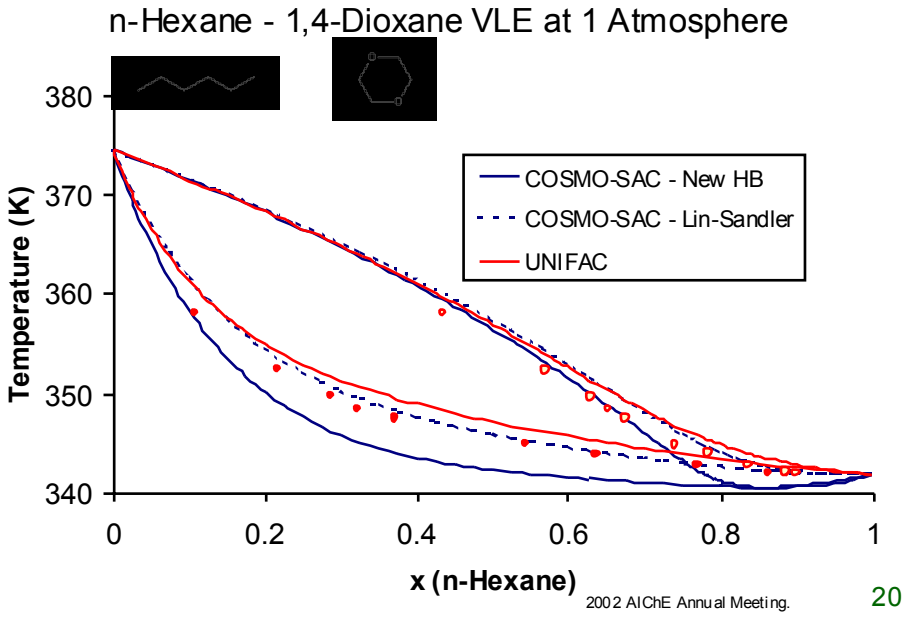


Results – VLE-2

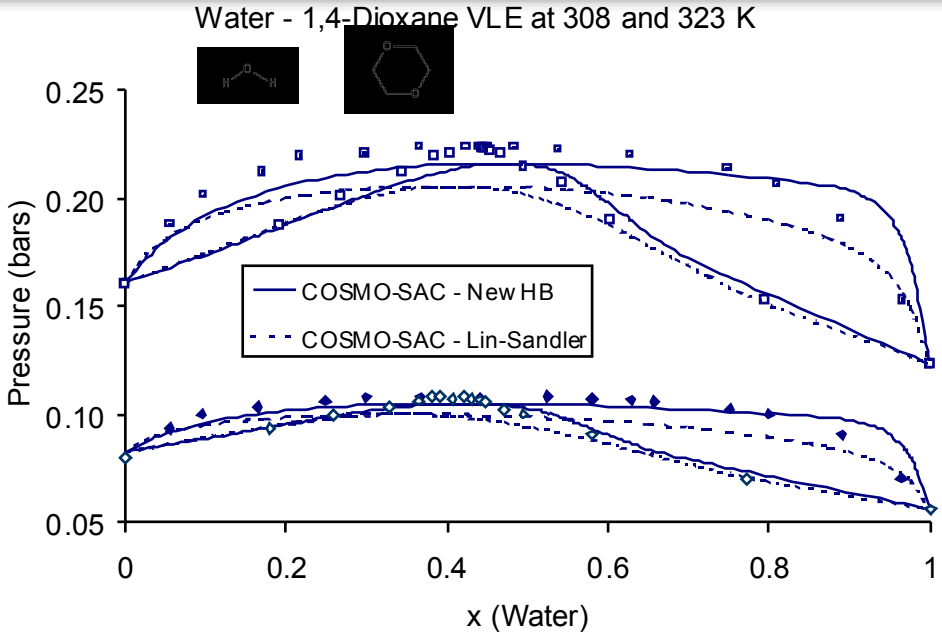


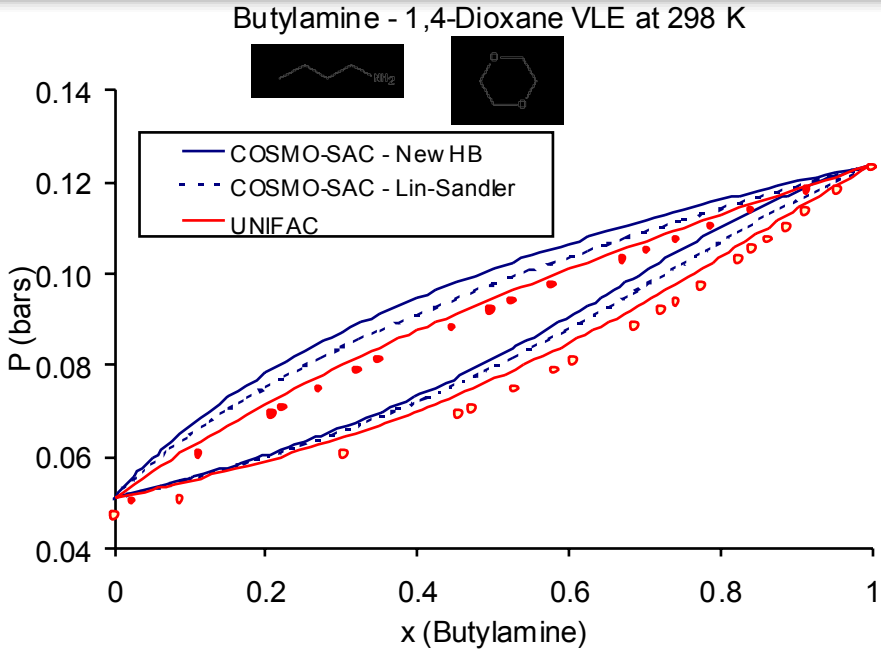


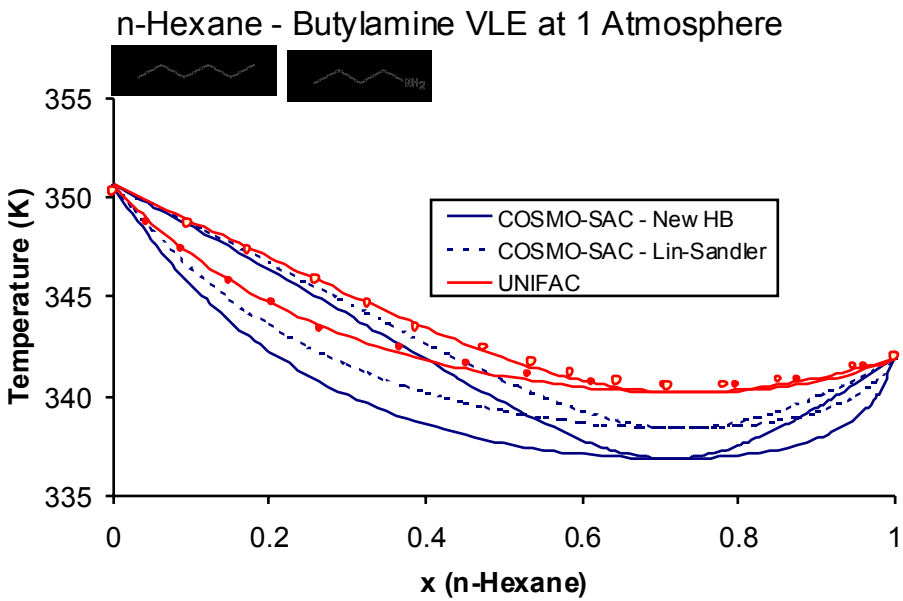


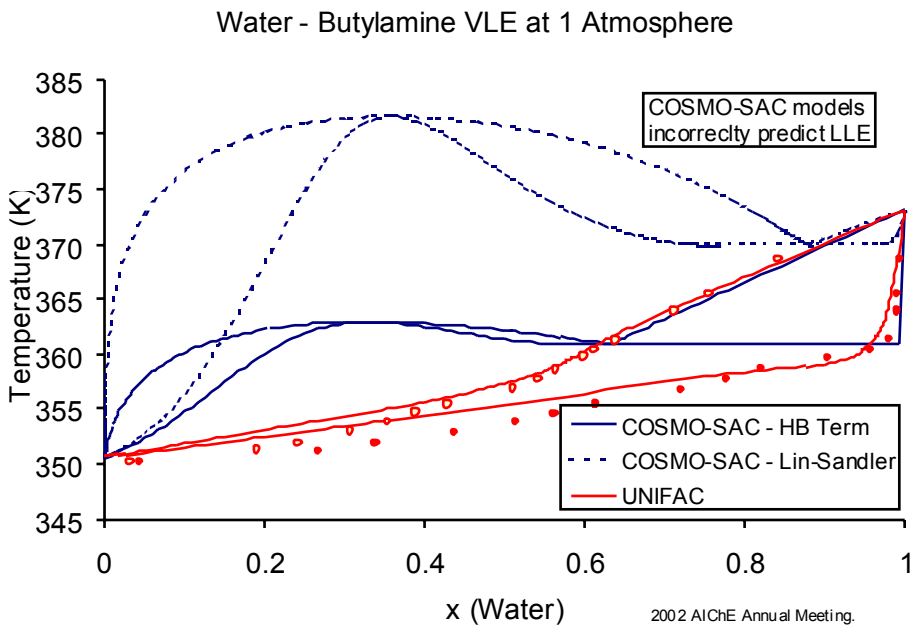


Results – VLE-3

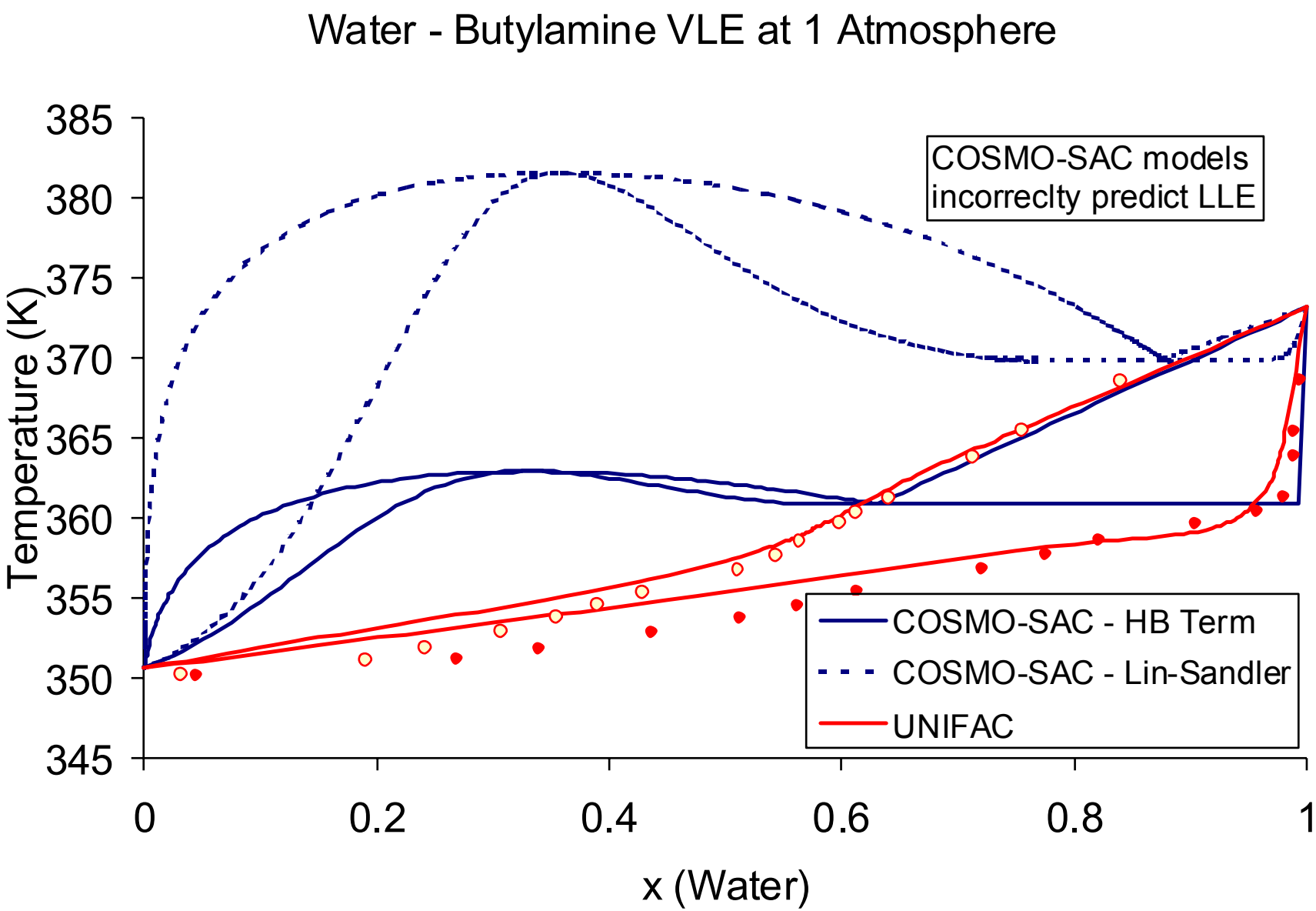




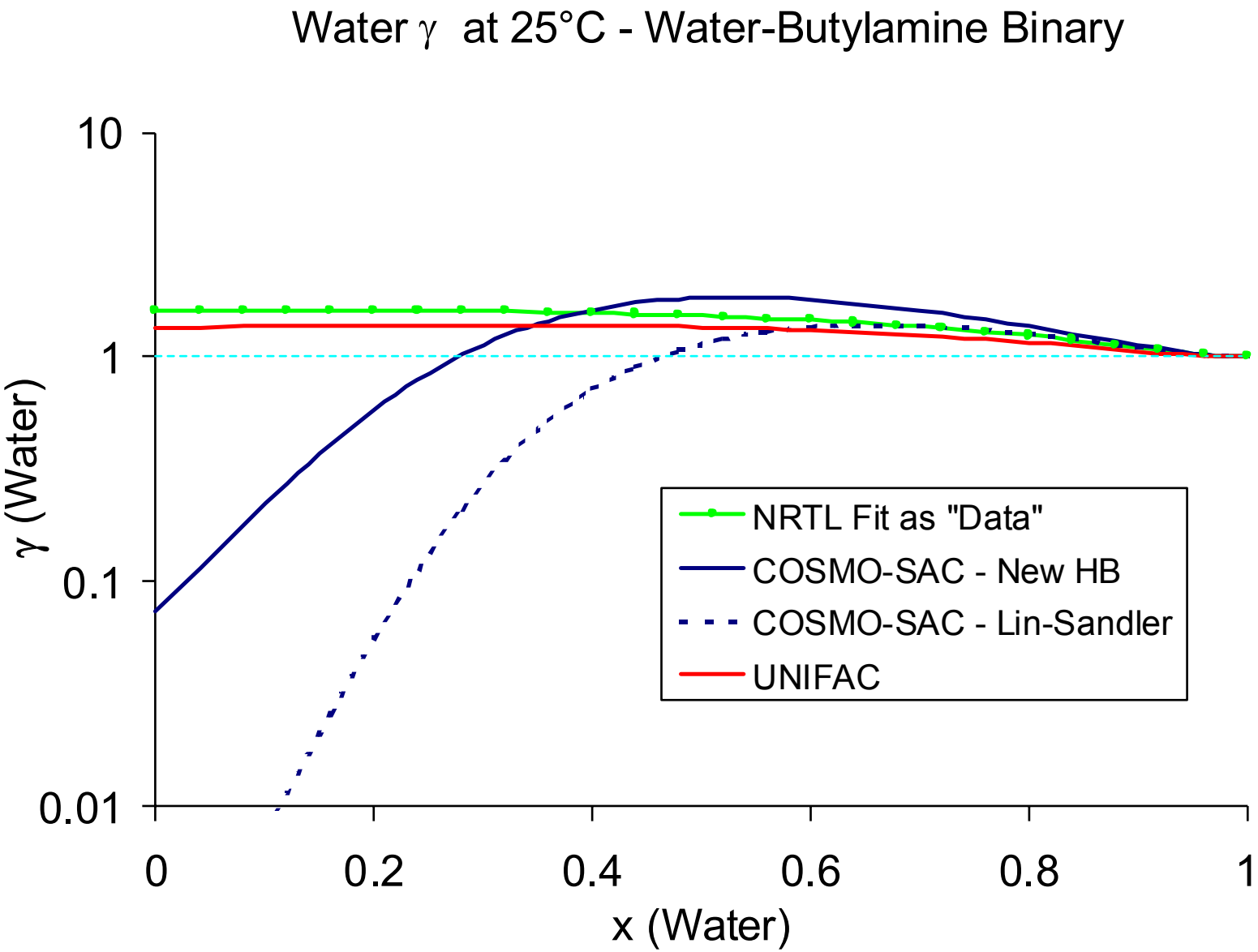




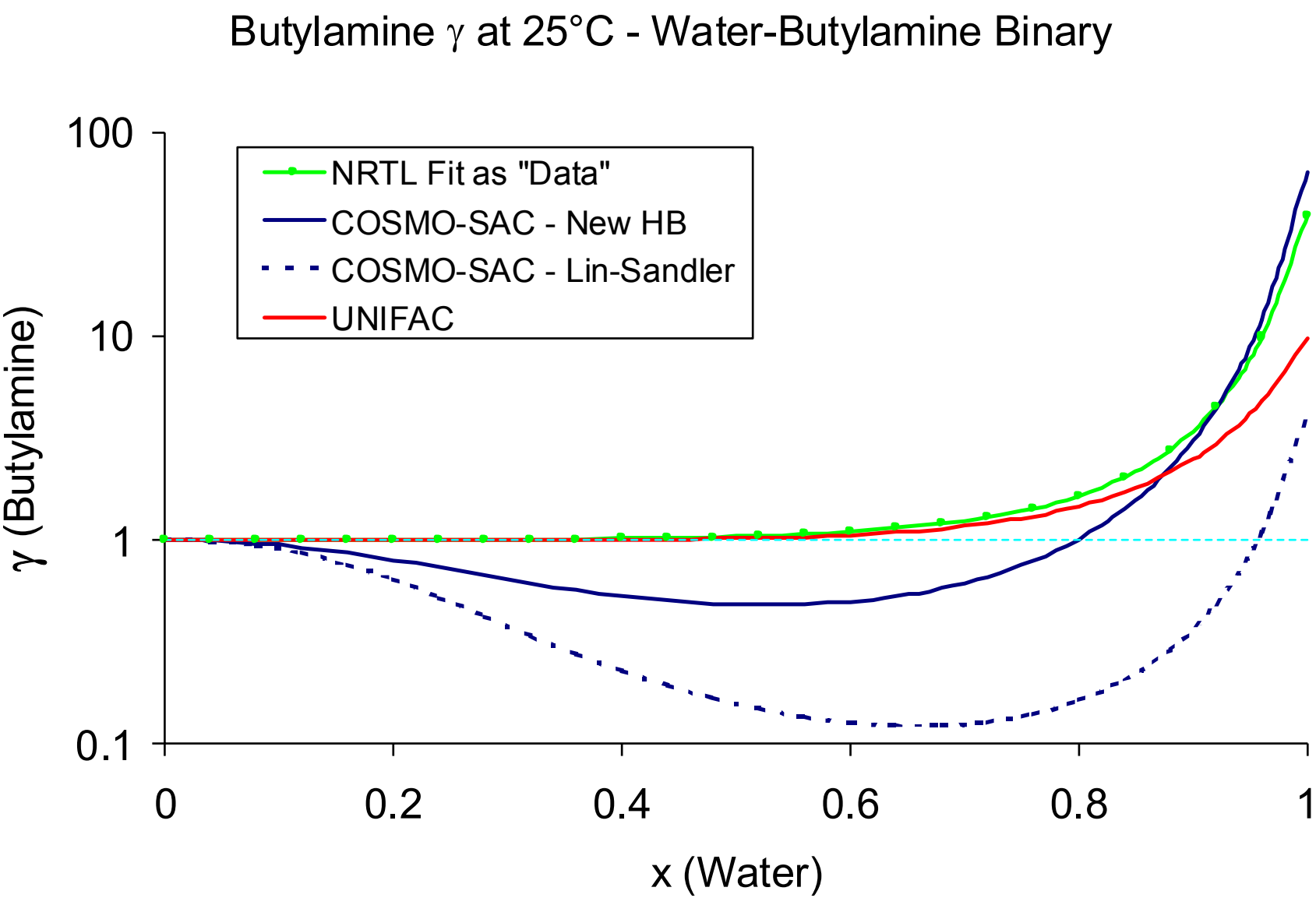
Results – Water-Butylamine



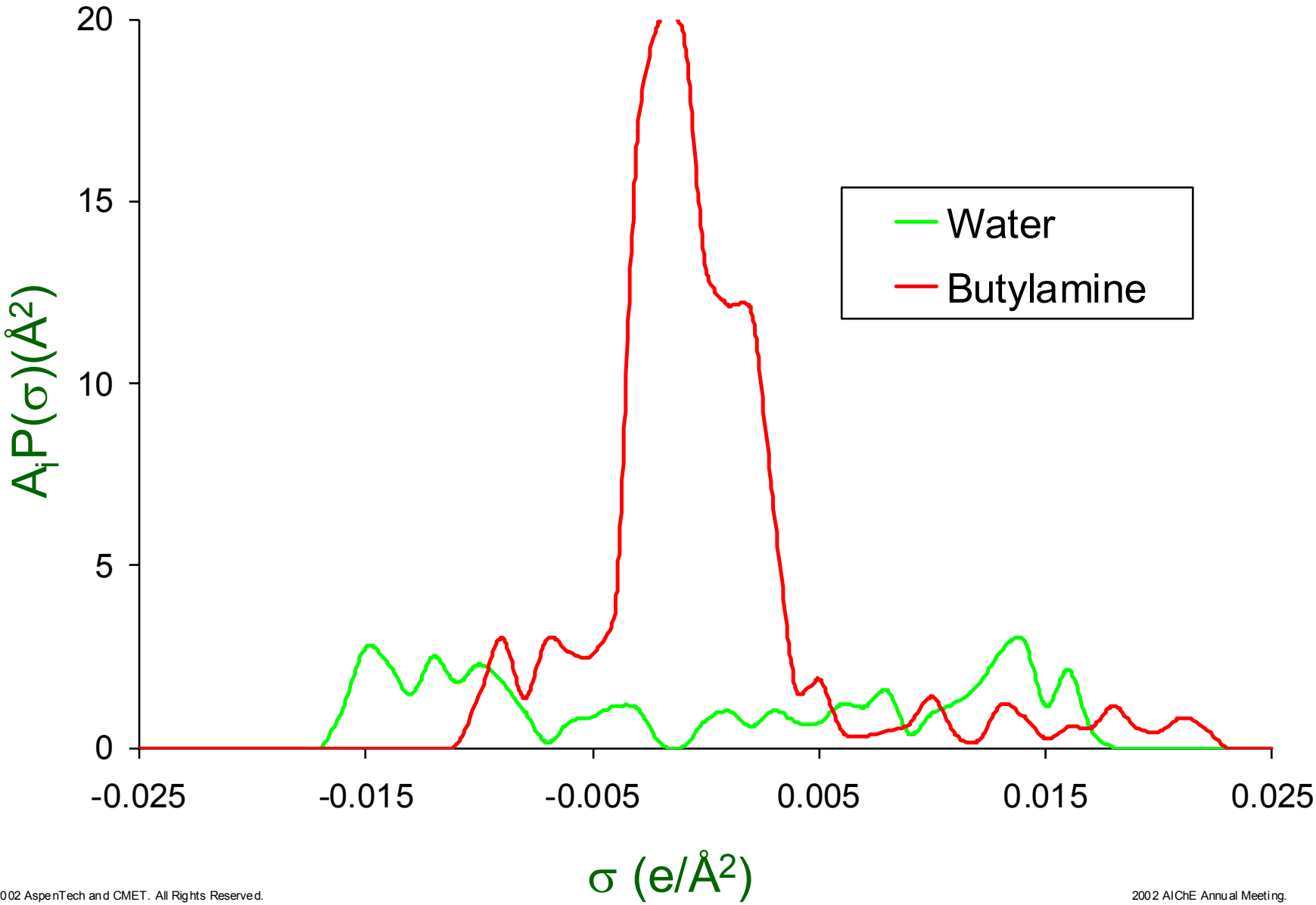
Water-Butylamine γ



Water-Butylamine γ



Selected σ–Profiles



Summary of Results

- COSMO-SAC generally predicts reasonable results
- The proposed HB term gives better results for strongly nonideal systems (e.g., LLE), at some expense of less ideal systems
- Results are sensitive to exchange energy – potential for improvement
- Exception is water-butylamine – amines are difficult to model with continuum solvation methods
- UNIFAC models perform well for most tested systems, except 1,4-dioxane

Conclusions

- COSMO-SAC performs remarkably well given the few parameters and its early stage of development
- UNIFAC performs well, but its limitations are known and the number of parameters is very large
- COSMO-SAC and related quantum based methods are viable predictive tools, but further development is needed – and we enthusiastically encourage further research in this area