



ADVANCED PROCESS MODELLING FORUM

LONDON

20–21 APRIL 2016



gSAFT

Advances in thermodynamic modelling

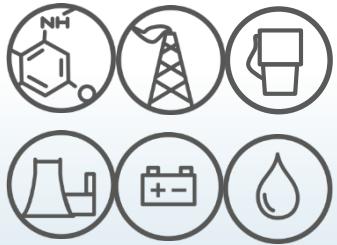
Dr Thomas Lafitte – Senior Scientist



gPROMS product family



"Fluids processing world"



g|PROCESS
gPROMS
ProcessBuilder
Process MLs

g|WATER

Water MLs

g|UTILITIES

Utilities MLs

g|CCS

CCS MLs

g|POWER

Power MLs

g|OILFIELD

Oilfield MLs

"Formulated products world"

g|FORMULATE
gPROMS
FormulatedProducts



Crystallization MLs

g|CRYSTAL

Solids MLs

g|SOLIDS

Oral absorption MLs

g|COAS

g|FLARE *

Flare &
depressurization MLs

g|FUELCELL

Fuel cell MLs

General
mathematical
modeling

g|MODEL

gPROMS ModelBuilder
provides essentially
the full platform
functionality



The gPROMS platform
Equation-oriented modelling & solution engine



* Primarily used internally by PSE for delivery of services

gSAFT in gPROMS

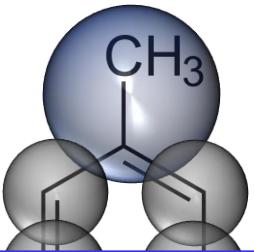


SAFT- γ Mie equation of state molecular model – I

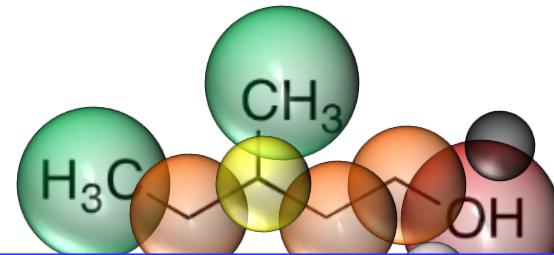


- Each molecule comprises one or more functional groups

toluene



alcohols



Molecular Physics, 2014
Vol. 112, No. 17, 2339–2364, <http://dx.doi.org/10.1080/00268976.2014.910316>



INVITED ARTICLE

Modelling of the thermodynamic and solvation properties of electrolyte solutions with the statistical associating fluid theory for potentials of variable range

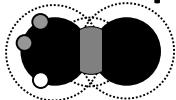
Jens M.A. Schreckenberg[†], Simon Dufal, Andrew J. Haslam, Claire S. Adjiman, George Jackson and Amparo Galindo*

Qatar Carbonates and Carbon Storage Research Centre and Centre for Process Systems Engineering, Department of Chemical Engineering, Imperial College London, University of London, London, UK

(Received 22 December 2013; accepted 20 March 2014)

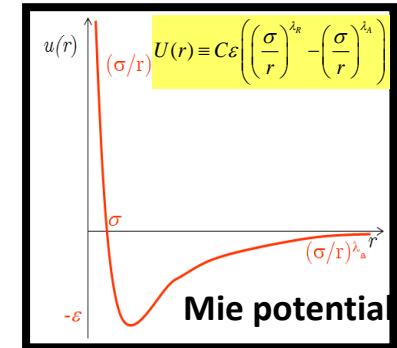
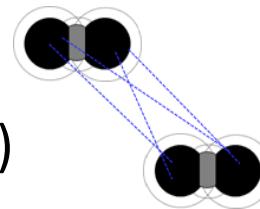
SAFT- γ Mie equation of state molecular model – II

- Each functional group comprises one or more identical segments

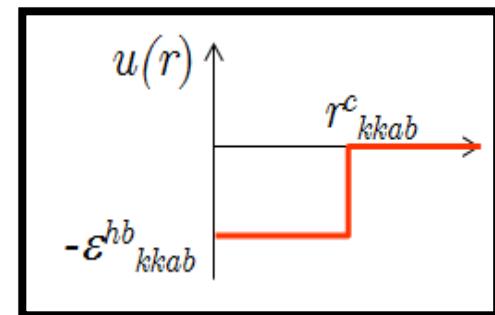
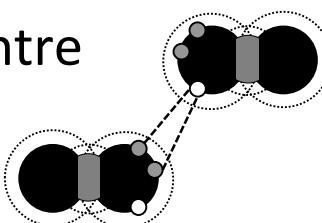


- Interactions between segments

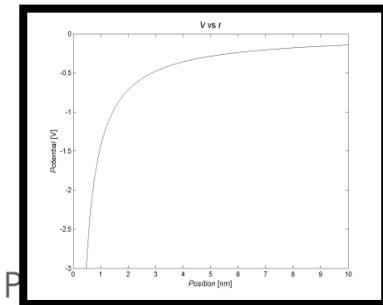
- dispersion/repulsion (van der Waals) forces



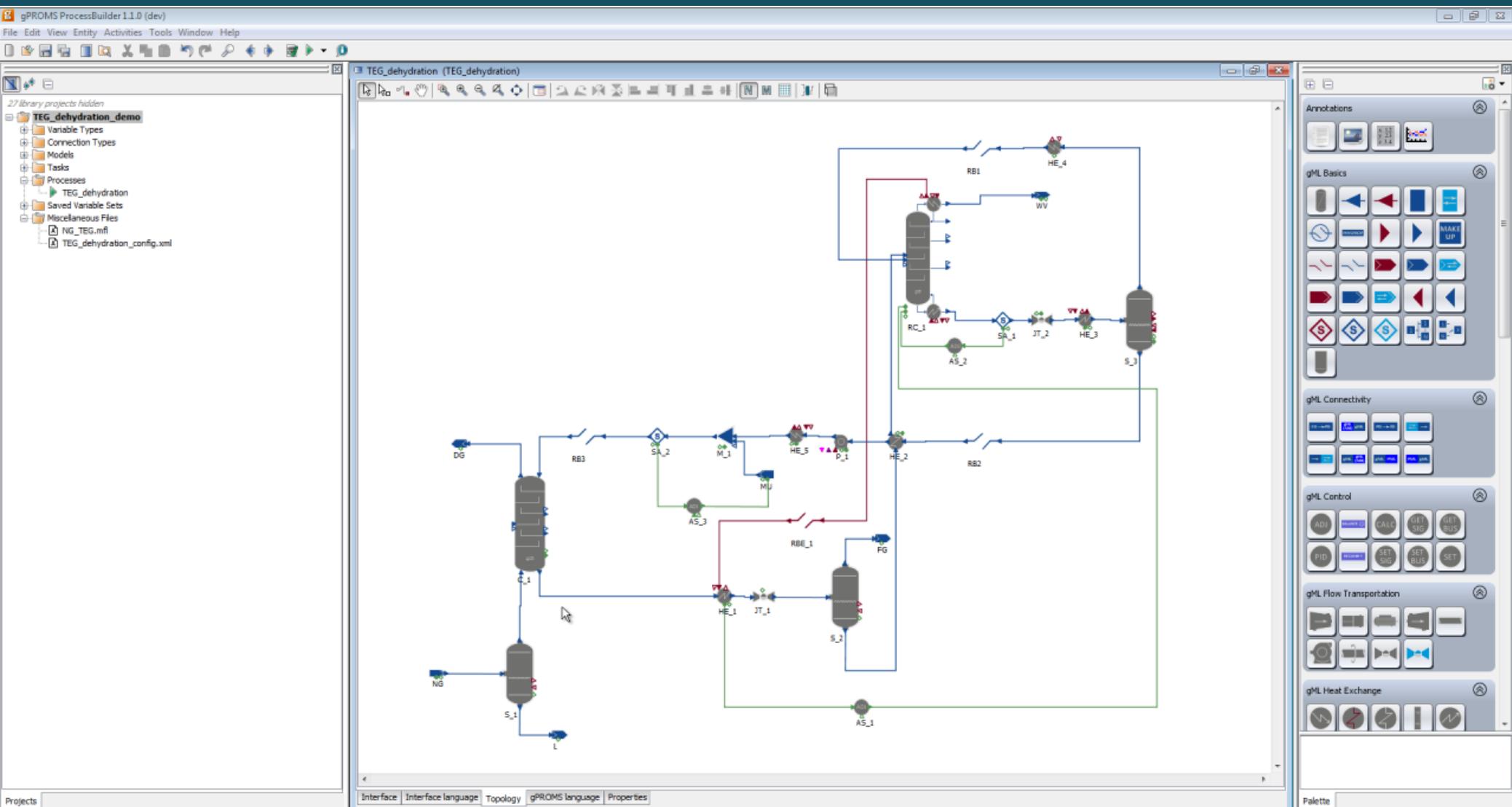
- hydrogen bonding via off-centre electron donor/acceptor ("association") sites



- ionic (coulombic) forces



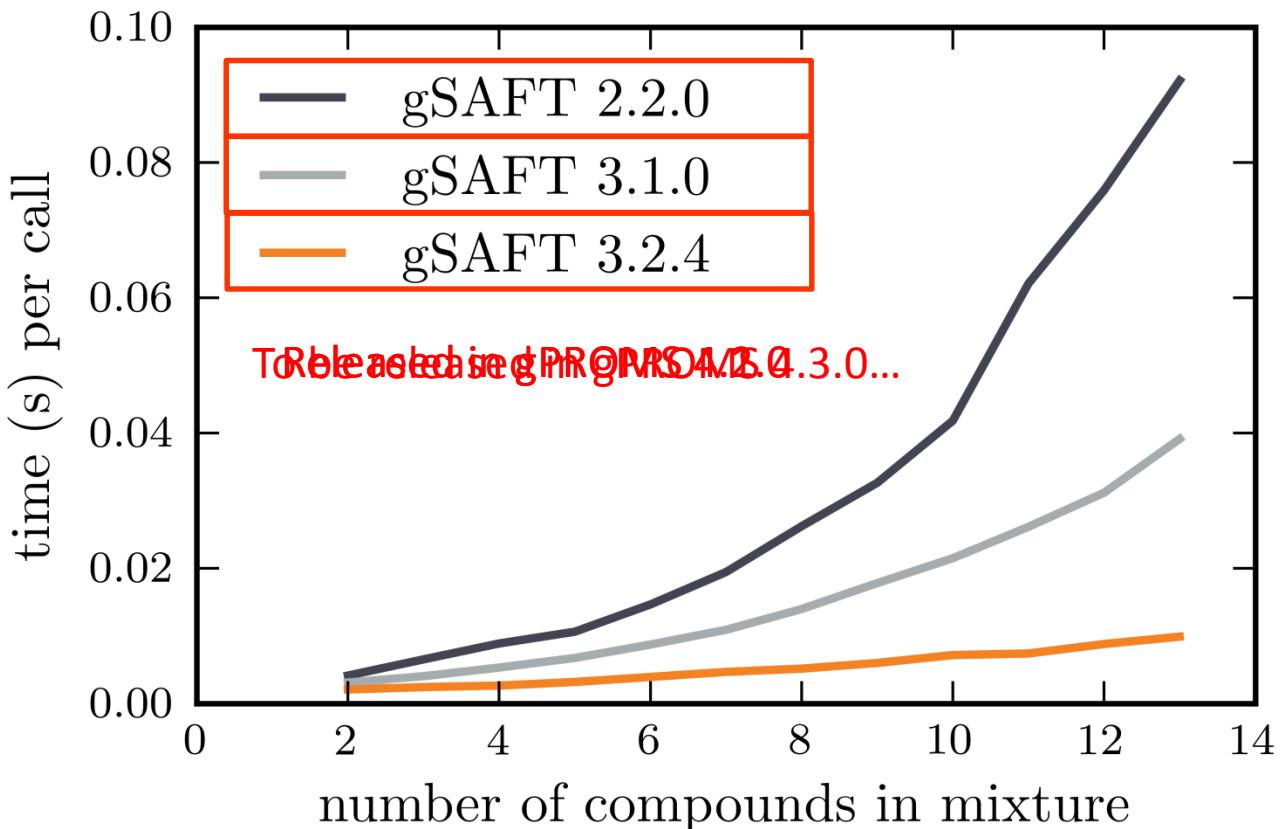
gSAFT in ProcessBuilder flowsheeting example



ADVANCED PROCESS MODELLING FORUM 2016

Performance improvements - I

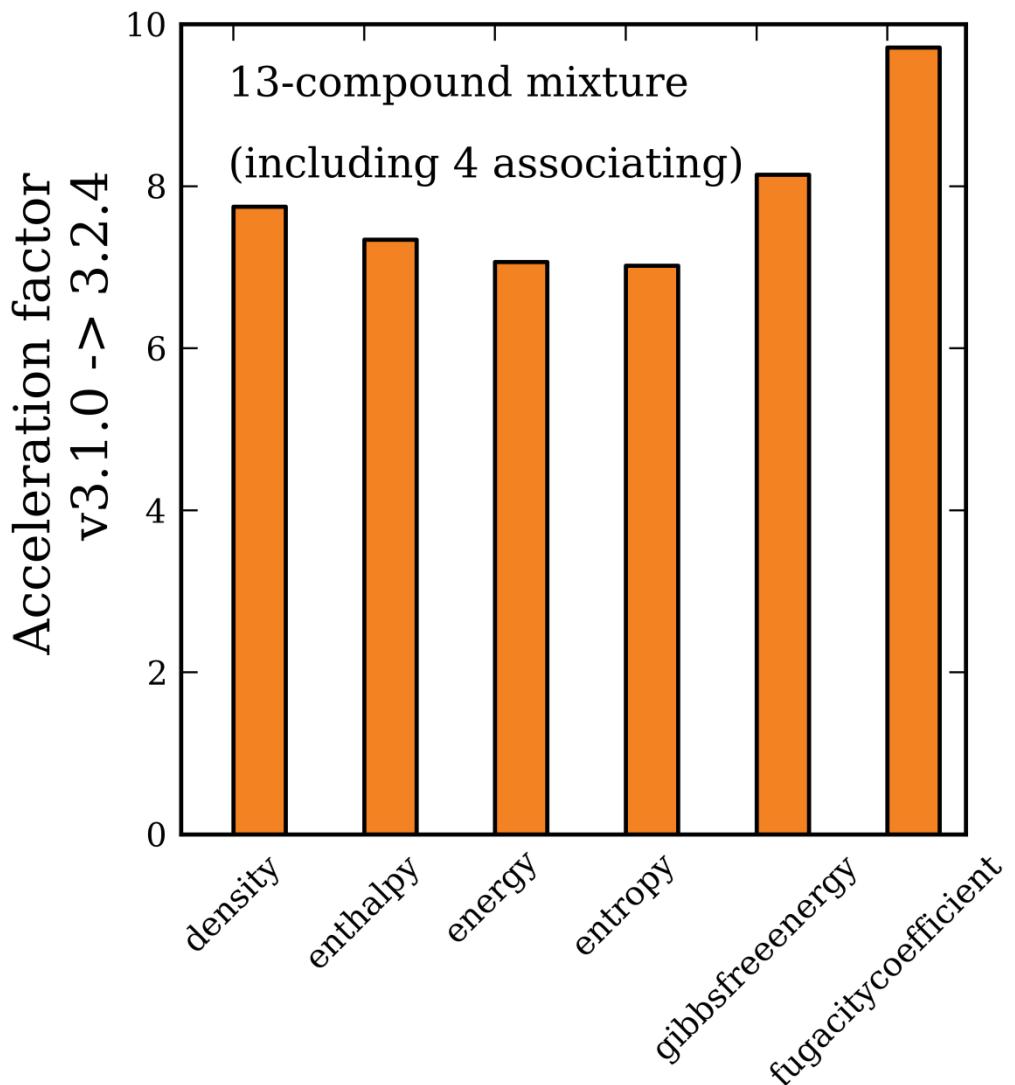
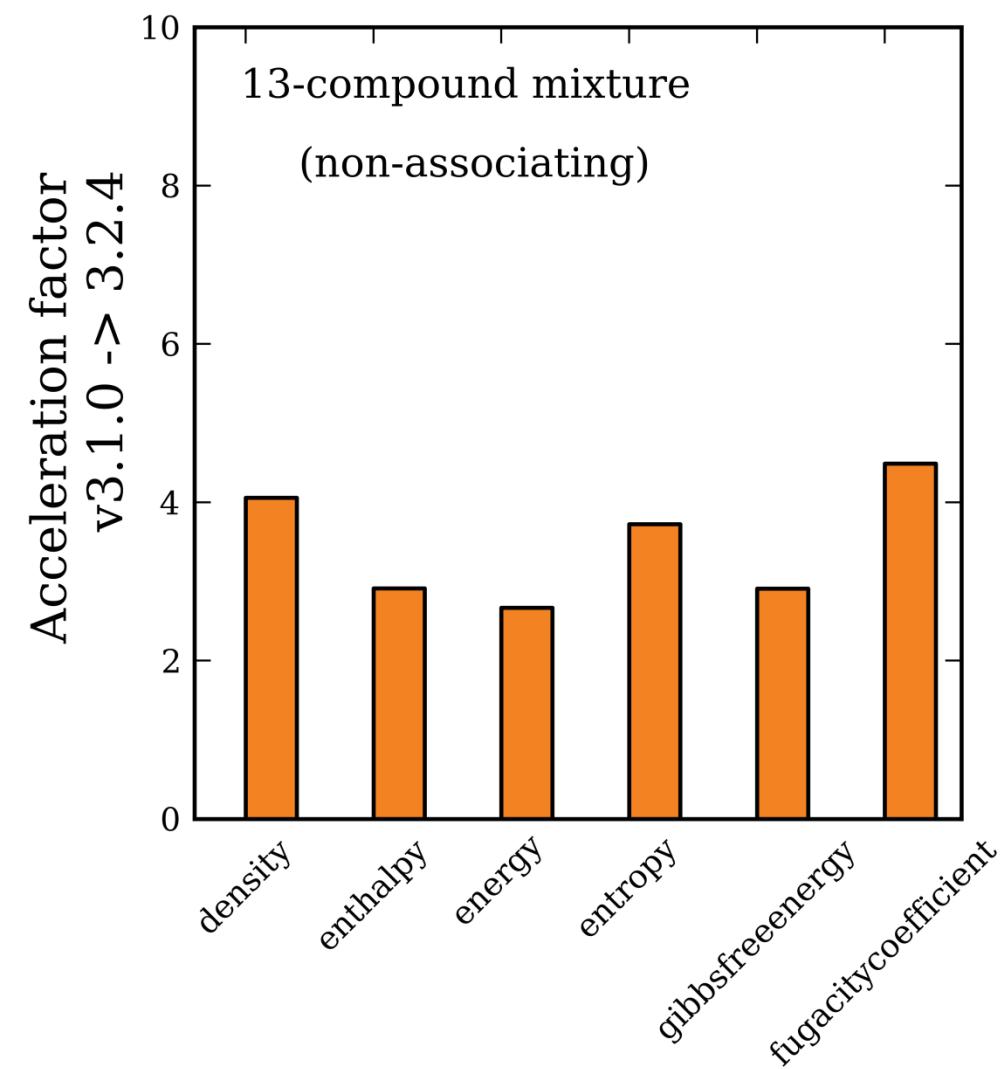
Phase equilibrium - Scaling with number of compounds



→Significantly improved scaling with number of compounds

Performance improvements - II

Single phase properties – acceleration factor from gPROMS v4.2 to v4.3



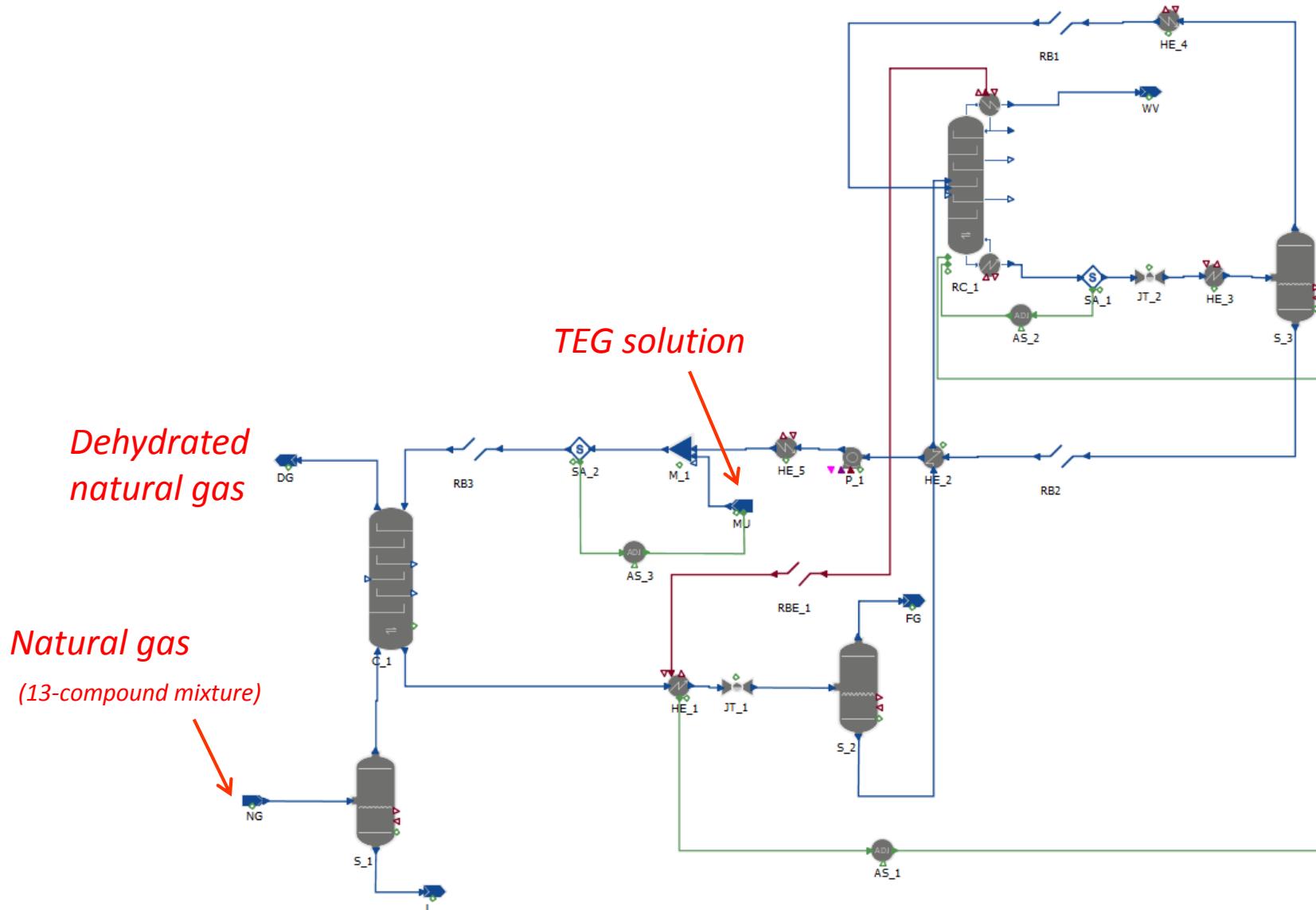
Application #1

Natural gas dehydration process using TEG



Application #1: TEG dehydration

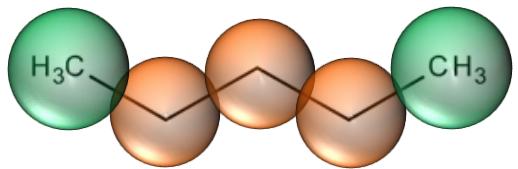
Process modelling



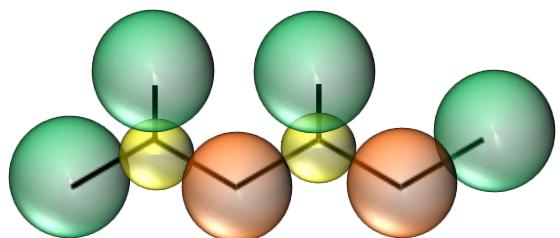
Application #1: TEG dehydration process

Material modelling

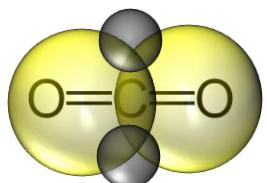
■ Alkanes



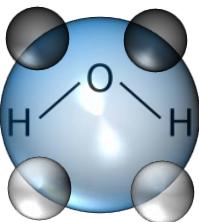
■ Branched alkanes



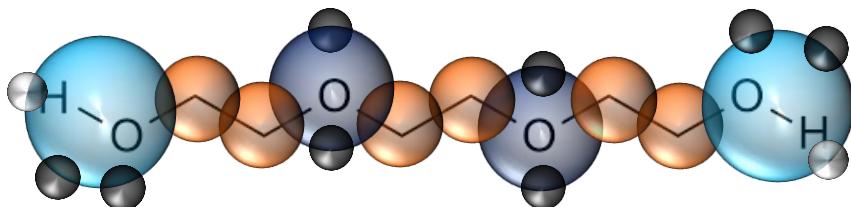
■ carbon dioxide



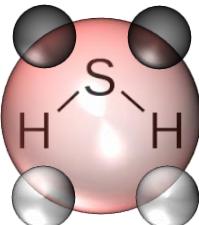
■ water



■ TEG



■ Hydrogen sulfide



■ methane

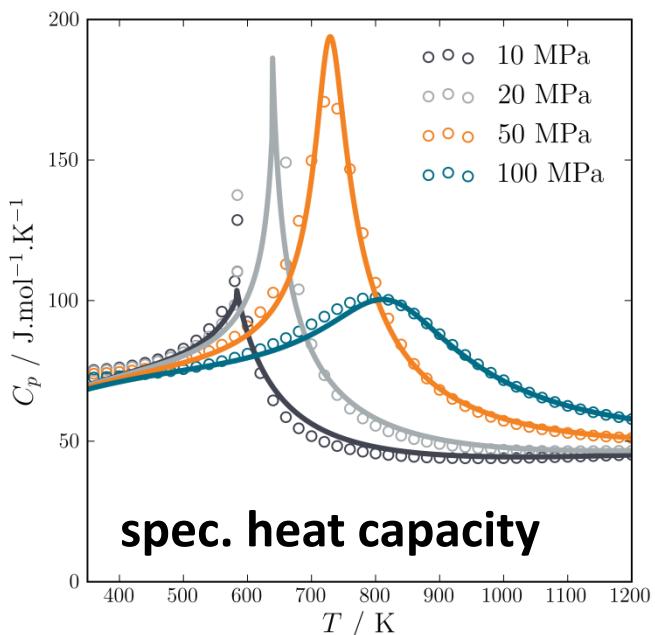
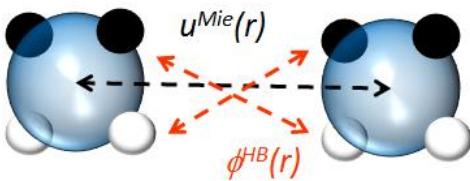
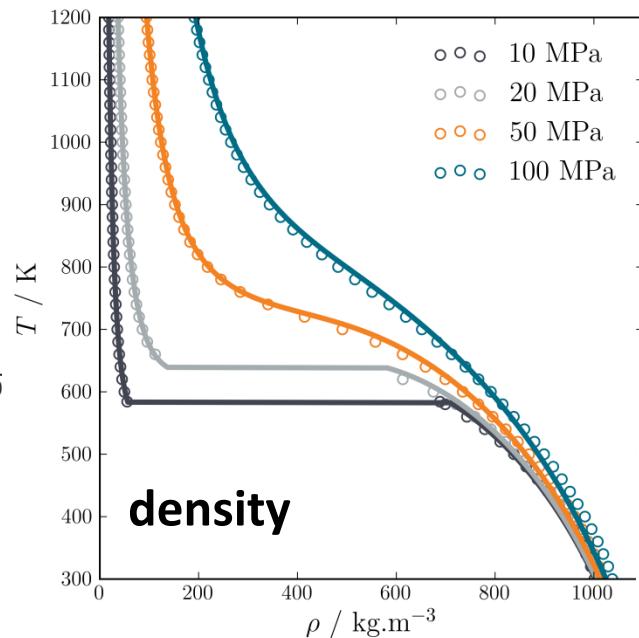
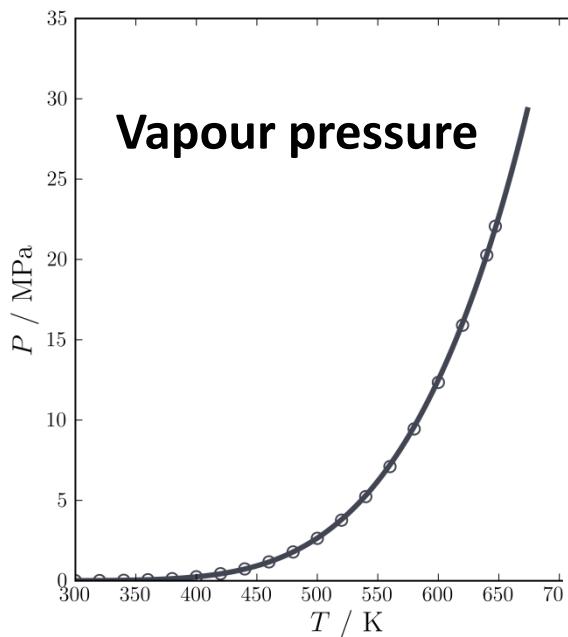


■ nitrogen



Application #1: TEG dehydration process

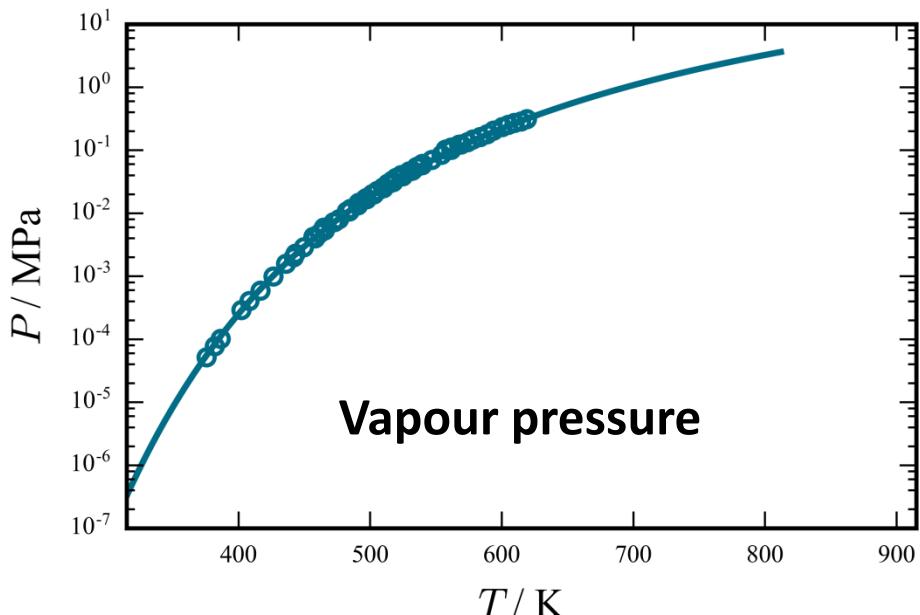
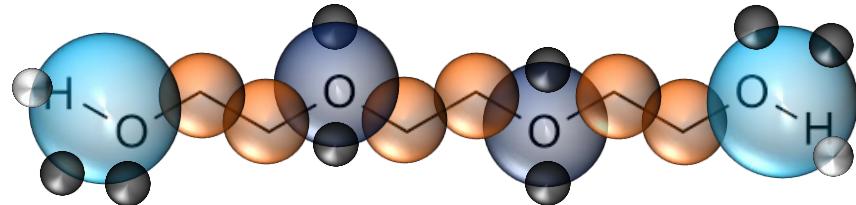
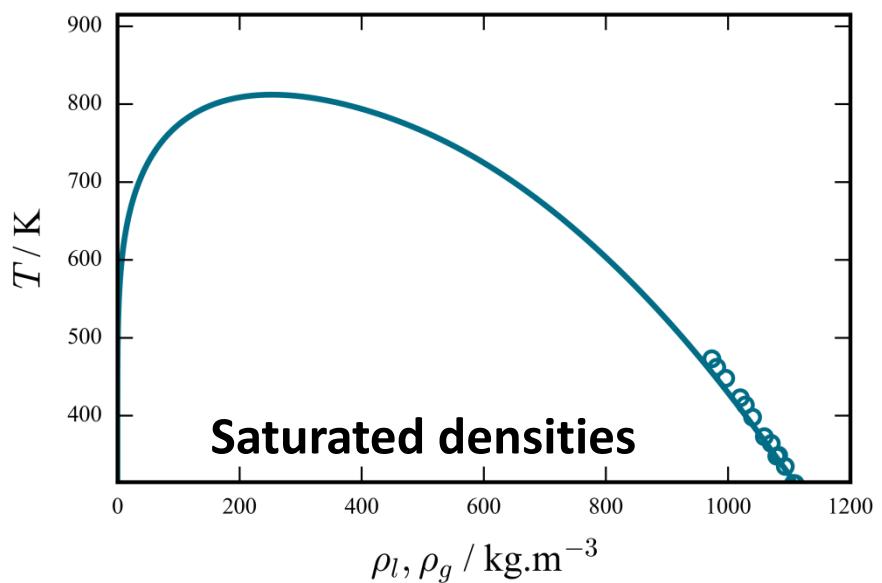
pure water properties



Experimental data : NIST Chemistry webbook

Application #1: TEG dehydration process

pure TEG properties

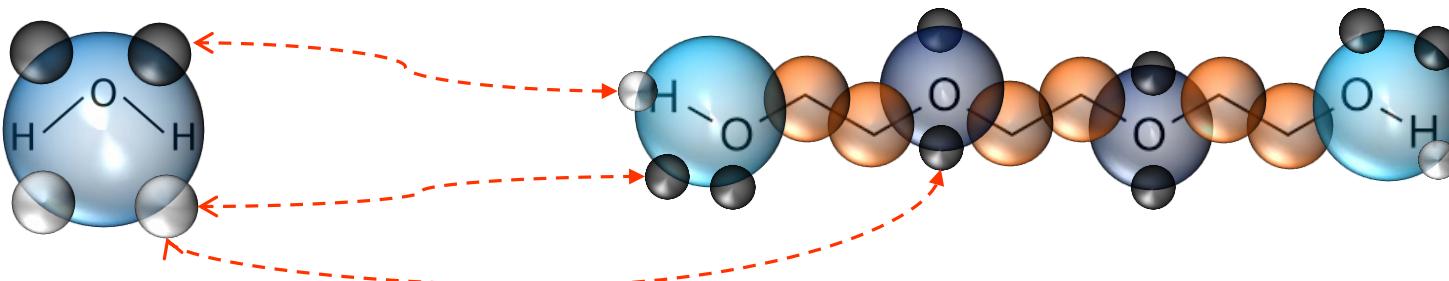


Experimental data:

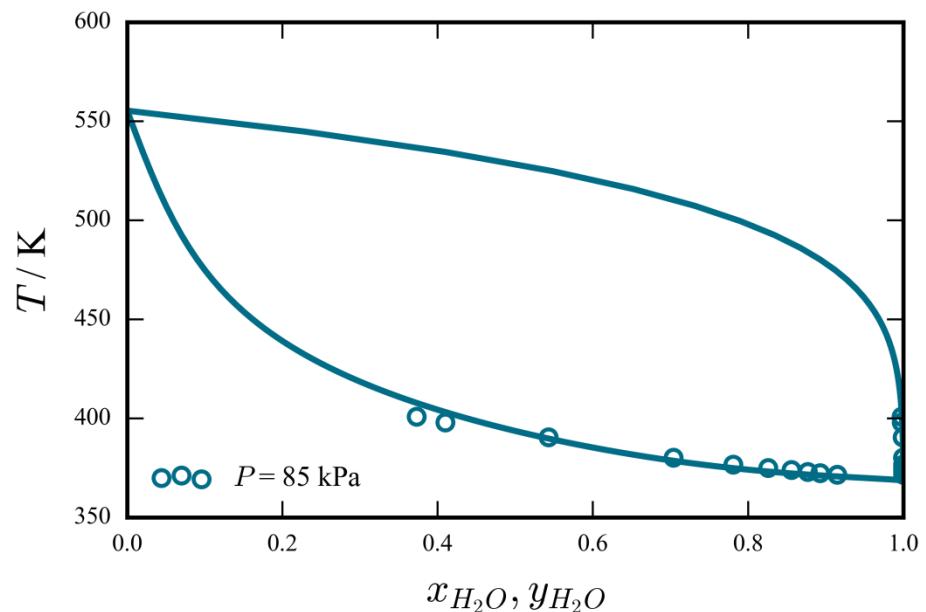
W. V. Steele et al., *J. Chem. Eng. Data*, **47**, 689 (2002)

Application #1: TEG dehydration process

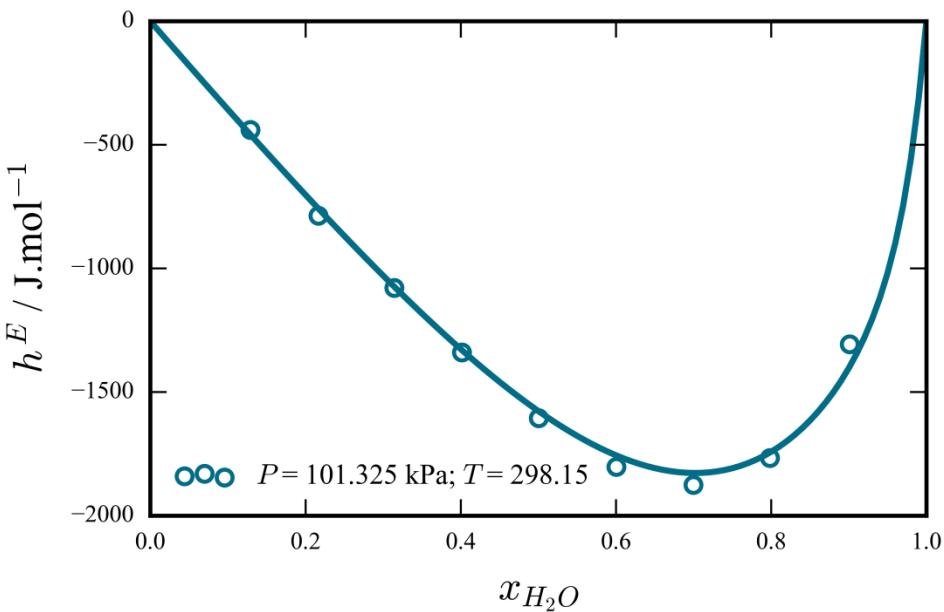
water + TEG mixture properties



■ Vapour-liquid equilibrium

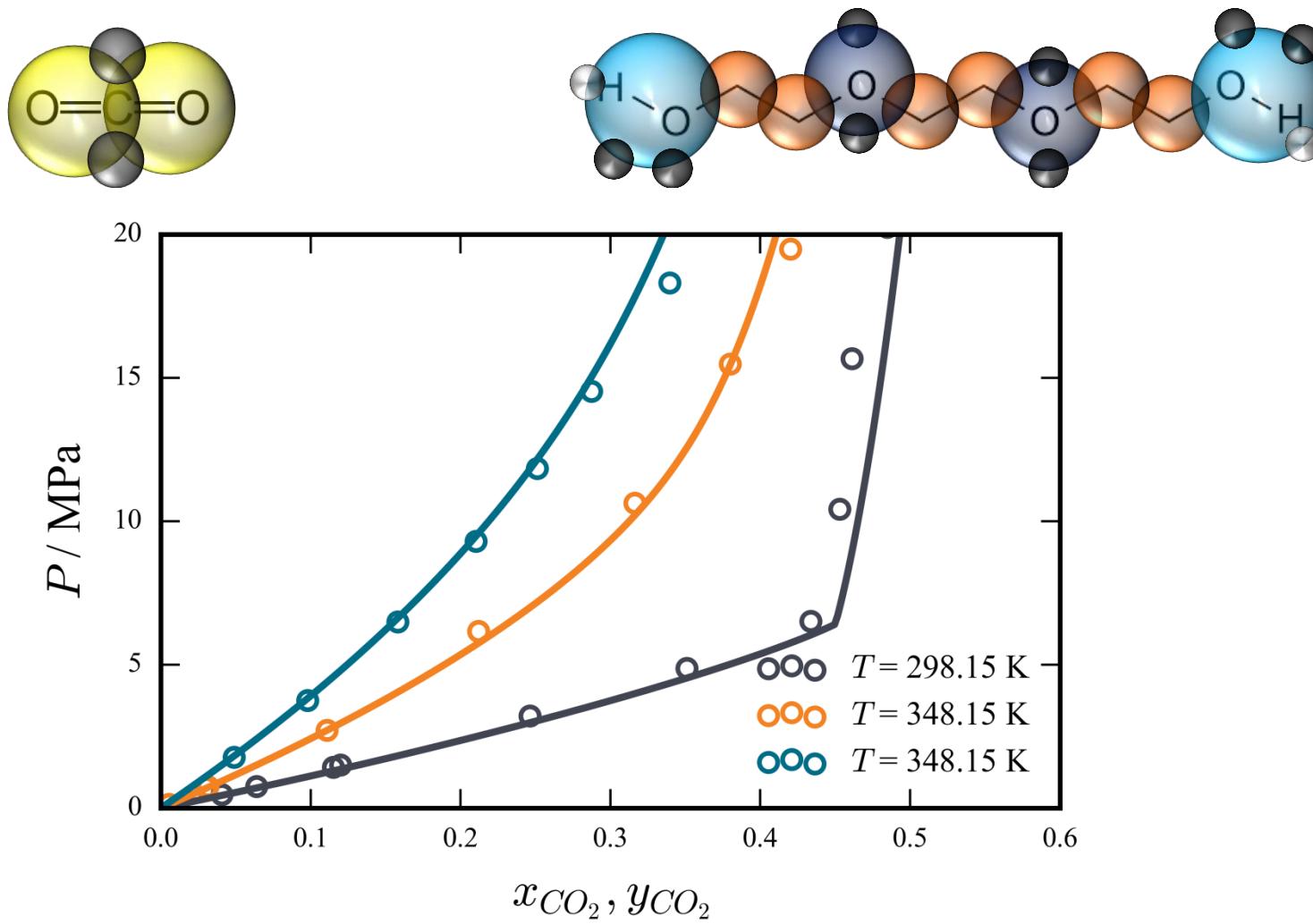


■ Excess enthalpy



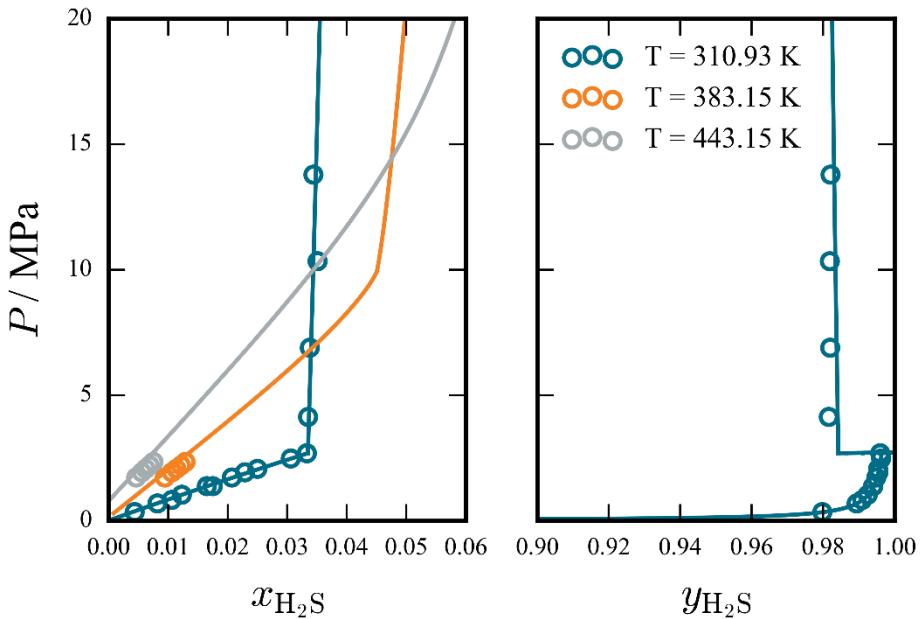
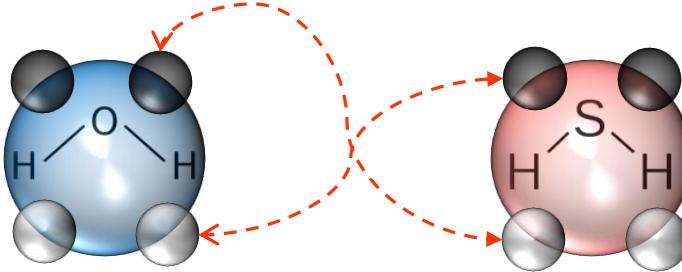
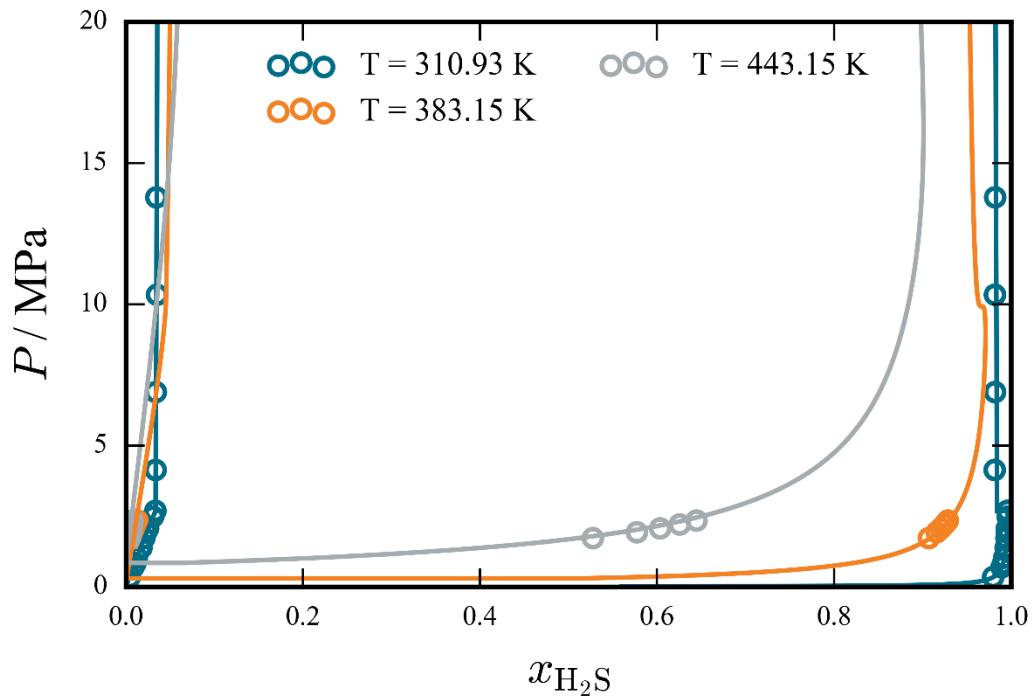
Application #1: TEG dehydration process

TEG + CO₂ mixture properties



Application #1: TEG dehydration process

water + H₂S mixture properties

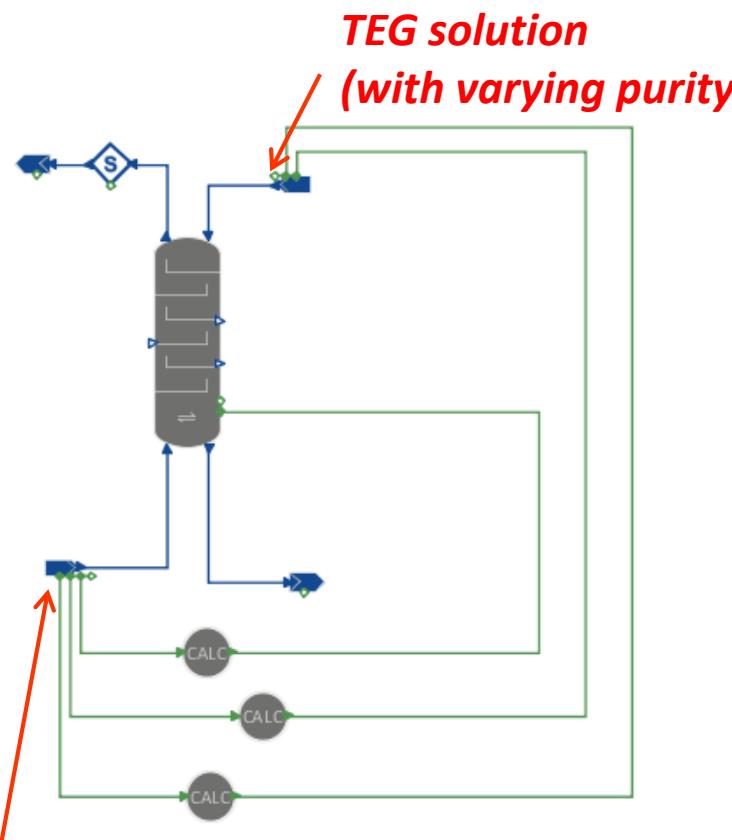


Experimental data :

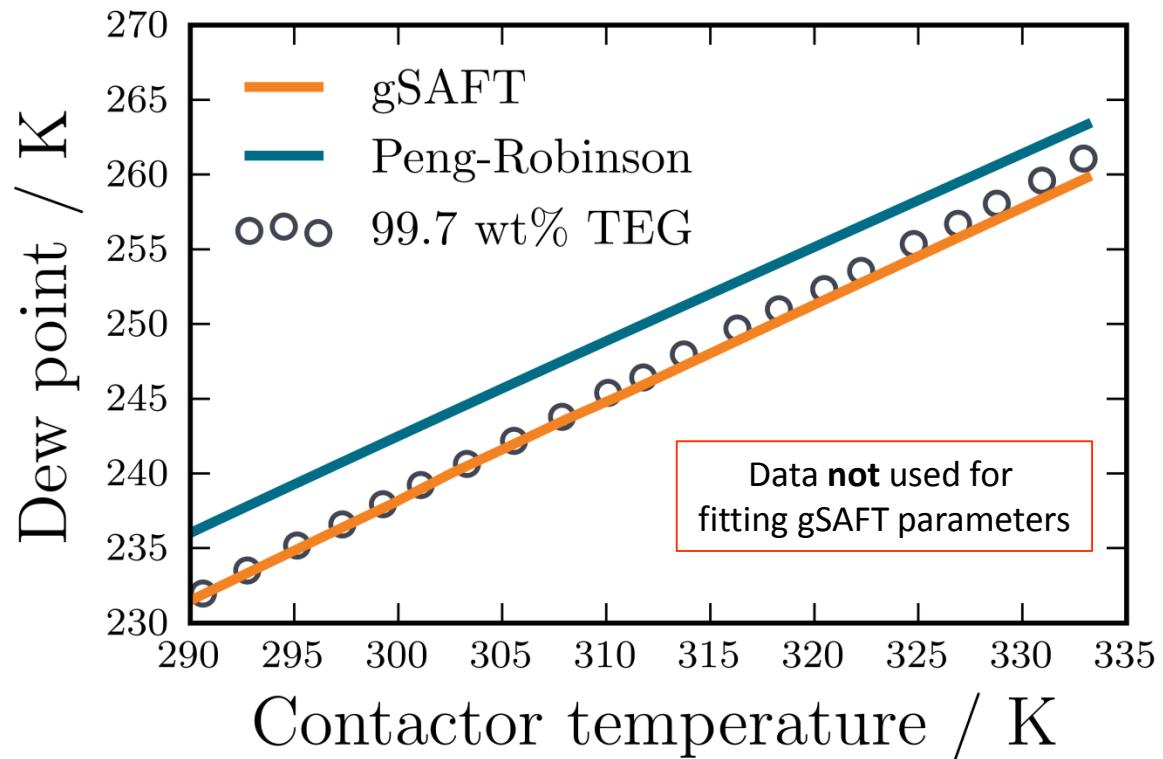
- F.T. Selleck, L.T. Carmichael, and B.H. Sage, *Ind. Eng. Chem.* **44**, 2219 (1952).
 P.C. Gillespie and G.M. Wilson, *Tech. Rep. (GPA Research Report RR-48)*, 1982.
 M.P. Burgess, and R.P. Germann, *AIChE J.* **15**, 272 (1969).

Application #1: TEG dehydration process

13-compound mixture – comparison with published data – I



*Natural gas
(13-compound mixture)
stream*

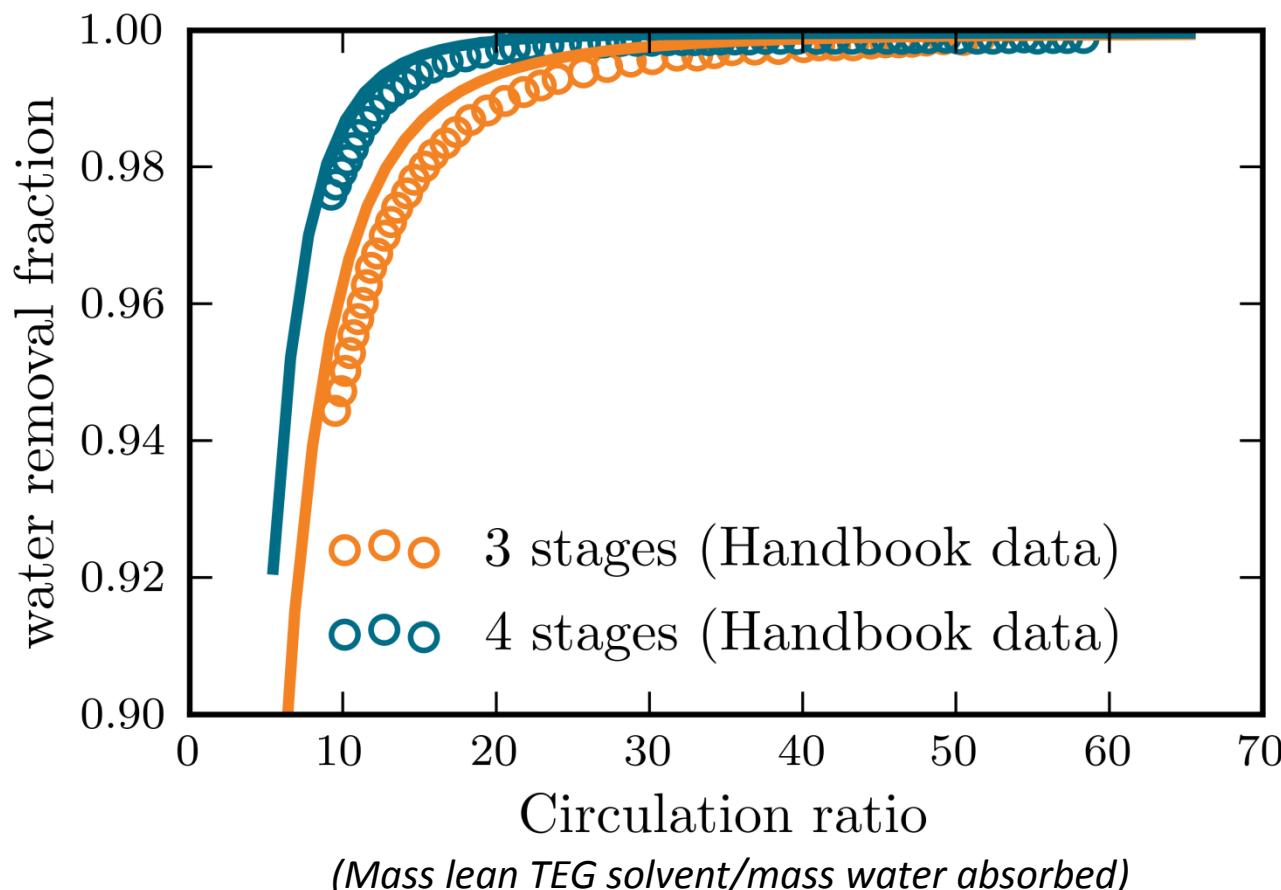


Experimental data :
GPSA Engineering Databook

Application #1: TEG dehydration process

13-compound mixture – comparison with published data – II

■ Absorber performance



Experimental data :

GPSA Engineering Databook

Application #2

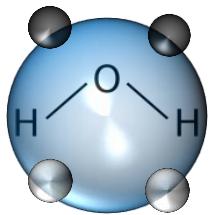
Phase diagram of micro-emulsions



Application #2: surfactant systems

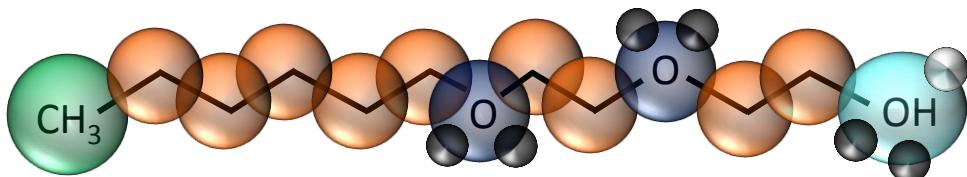
SAFT- γ Mie molecular models

- water



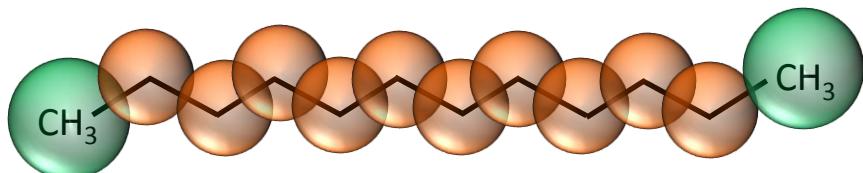
Same groups as in the
TEG dehydration example

- C_iE_j surfactant (*Polyoxyethylene alkyl ether*)



→ use same databank parameters
for completely different system

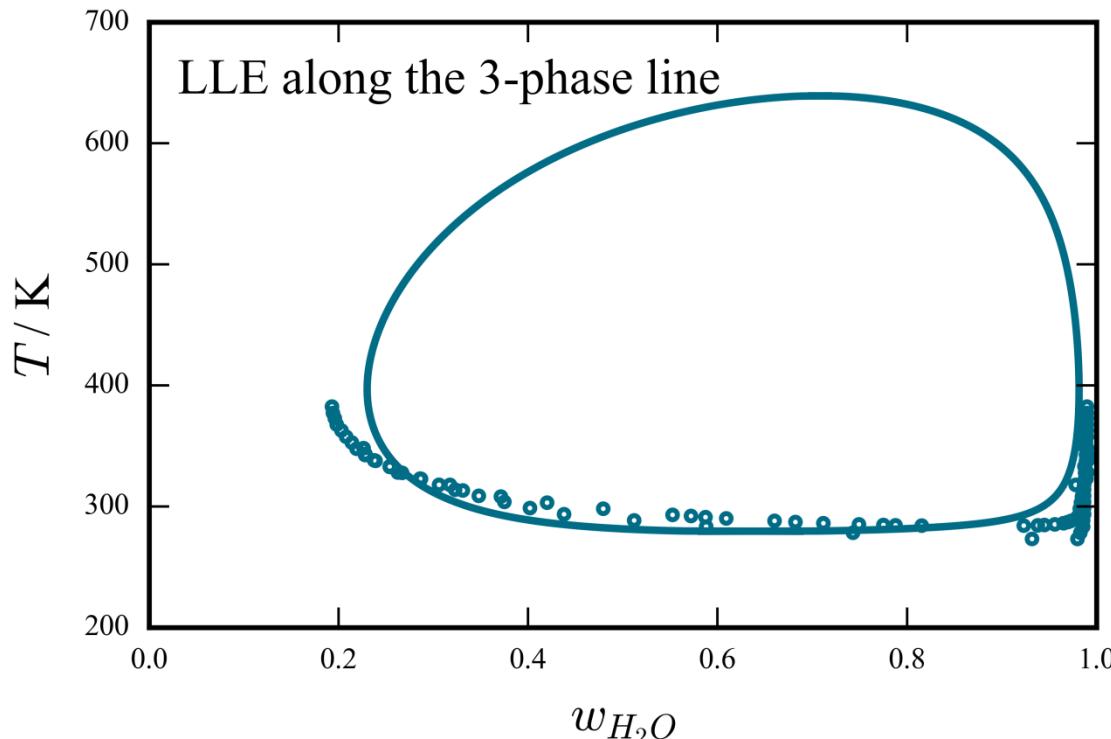
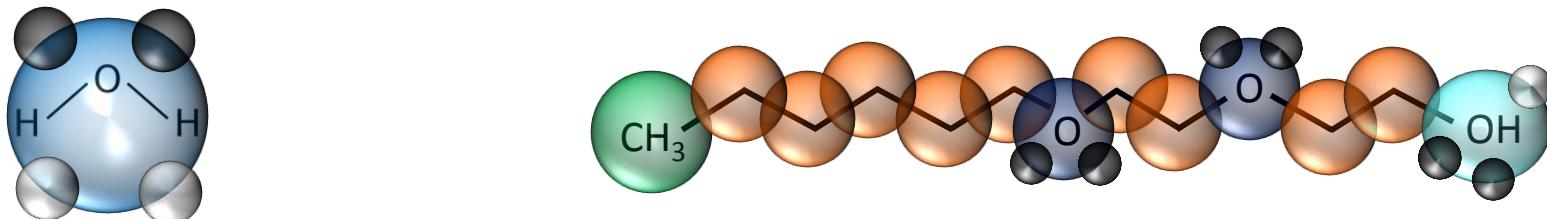
- n-dodecane



Predictive
methodology

Application #2: surfactant systems

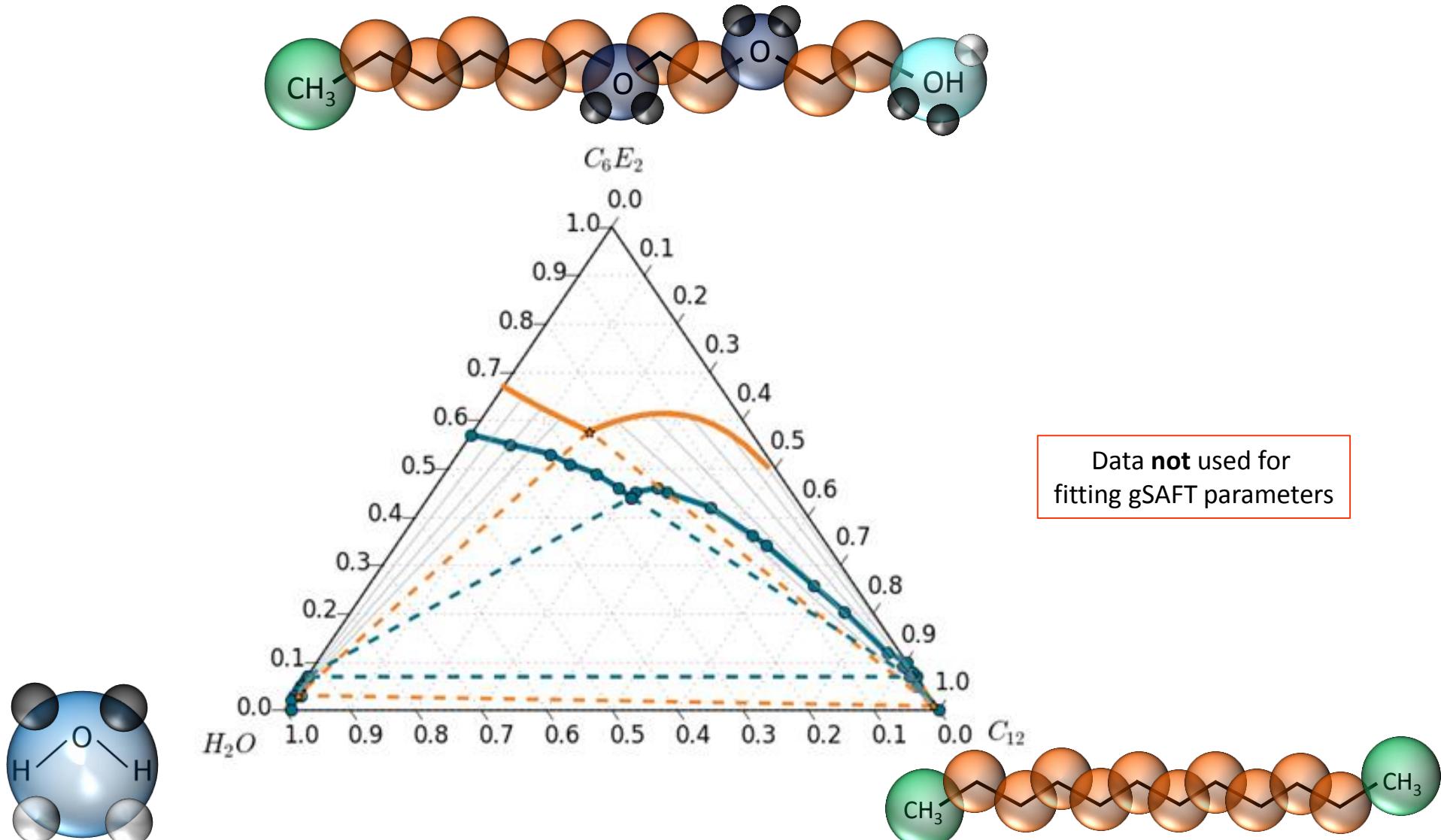
water + C₆E₂ liquid-liquid equilibrium



Data **not** used for
fitting gSAFT parameters

Application #2: surfactant systems

water + n-dodecane + C_6E_2 phase diagram



gSAFT for solid/liquid equilibrium



gSAFT for solid/liquid equilibrium

Computing chemical potentials

- Solid-liquid equilibrium condition:

$$\mu_i^s(T, P) = \mu_i^l(T, P, x)$$

Solid phase

Liquid phase



Can be approximated to be a pure phase

Complex function of temperature,
pressure, and composition

- Solid-liquid equilibrium condition:

$$\mu_i^s(T, P) = \mu_i^l(T, P, x)$$

Solid phase:

Requires readily available experimental data

Liquid phase:

Predicted with gSAFT

- Solid-phase chemical potential – method #1:

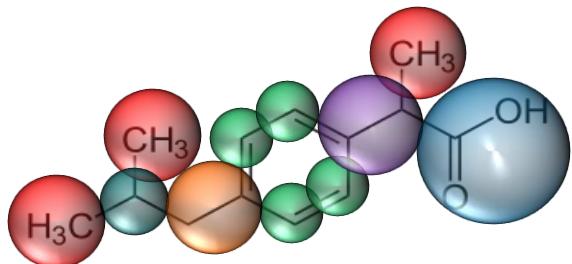
$$\mu_i^s(T) = \mu_i^l(T) + \Delta H^{l \rightarrow s}(T_m) \left(1 - \frac{T}{T_m} \right) + \int_{T_m}^T \Delta C_p^{l \rightarrow s}(T') dT' - T \int_{T_m}^T \frac{\Delta C_p^{l \rightarrow s}(T)}{T'} dT'$$

Required experimental data:

1. Melting temperature T_m
2. Melting enthalpy $\Delta H^{s \rightarrow l}$
3. Melting heat capacity $\Delta C_p^{s \rightarrow l}$

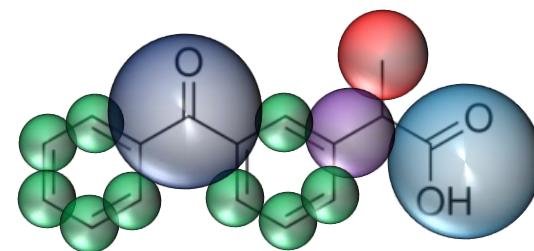
gSAFT for solid/liquid equilibrium

Method 1 (required data: T_m ; $\Delta H^{s \rightarrow l}$; $\Delta C_p^{s \rightarrow l}$)



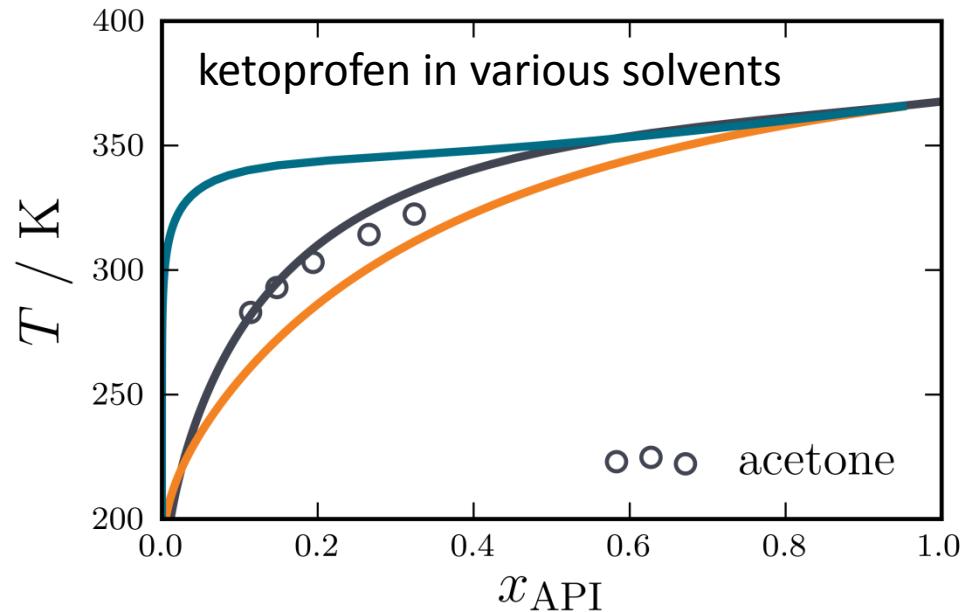
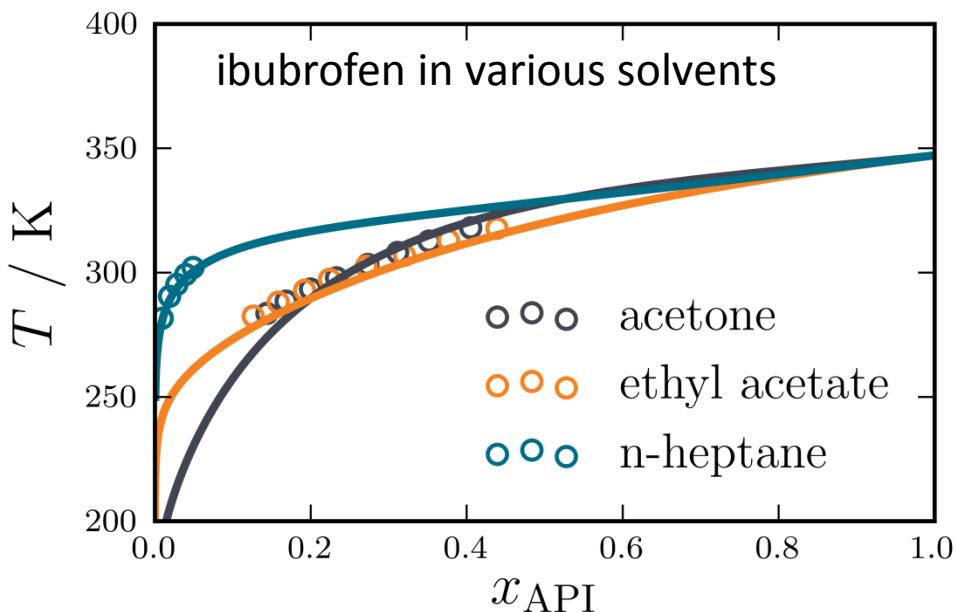
Ibuprofen

$$T_m = 347.15 \text{ K}; \Delta H^{s \rightarrow l} = 25500 \text{ J.mol}^{-1}; \Delta C_p^{s \rightarrow l} = 0 \text{ J.K}^{-1}.\text{mol}^{-1}$$



Ketoprofen

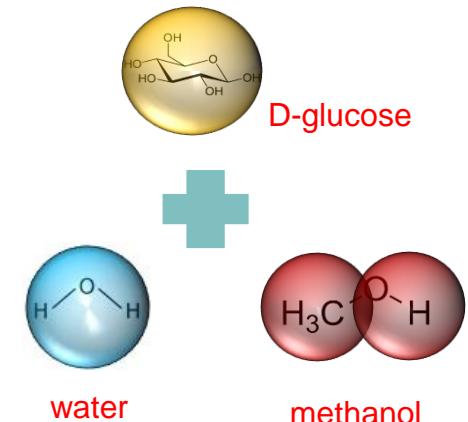
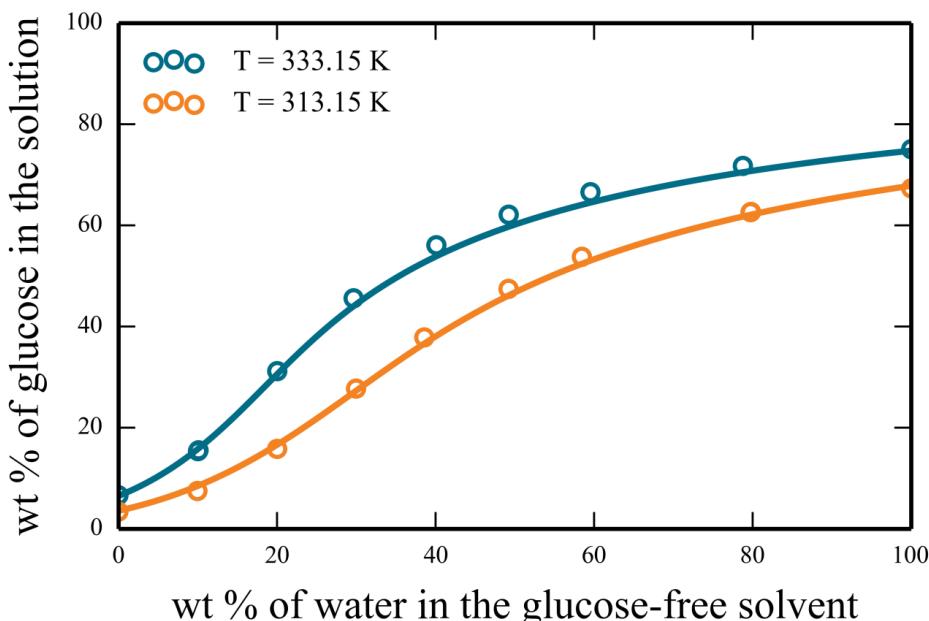
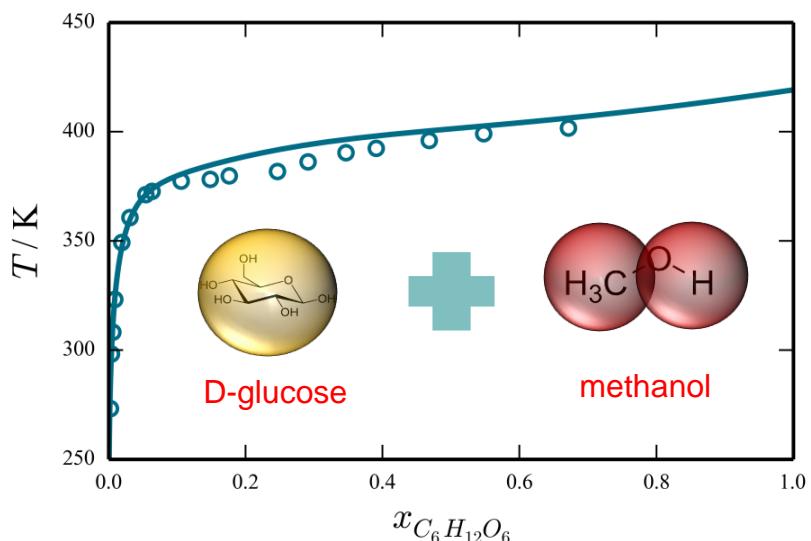
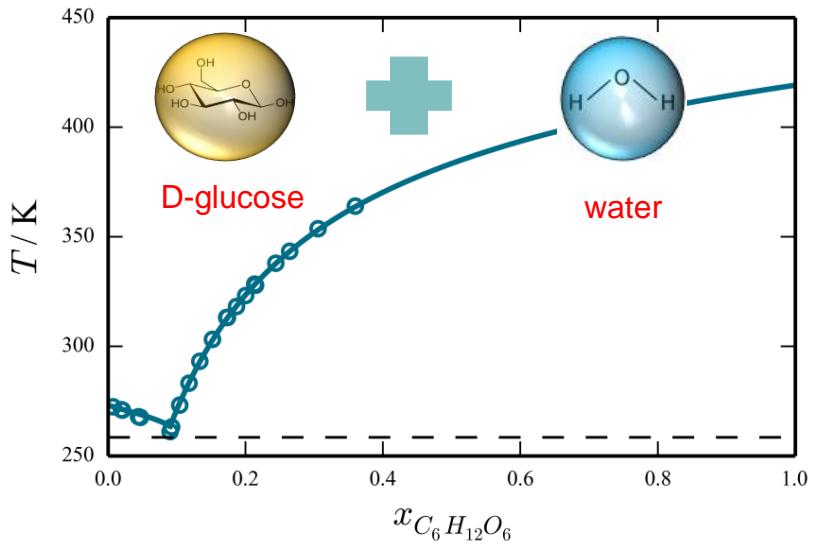
$$T_m = 367.65 \text{ K}; \Delta H^{s \rightarrow l} = 28245 \text{ J.mol}^{-1}; \Delta C_p^{s \rightarrow l} = 0 \text{ J.K}^{-1}.\text{mol}^{-1}$$



S. Gracin and A. C. Rasmussen, *J. Chem. Eng. Data*, **47**, 1379 (2002)

gSAFT for solid/liquid equilibrium

Method 1 (required data: T_m ; $\Delta H^{s \rightarrow l}$; $\Delta C_p^{s \rightarrow l}$)



- Solid-liquid equilibrium condition:

$$\mu_i^s(T, P) = \mu_i^l(T, P, x)$$

Solid phase:

Requires readily available experimental data

Liquid phase:

Predicted with gSAFT

- Solid phase chemical potential – method #2:

$$\mu_i^s(T) = \Delta H_i^{F,\Theta} - T\Delta S_i^{F,\Theta} + \int_{T^\Theta}^T c_{p,i}^s(T') dT' - T \int_{T^\Theta}^T \frac{c_{p,i}^s(T')}{T'} dT'$$

Required experimental data:

1. Enthalpy of formation $\Delta H_i^{F,\Theta}$
2. Entropy of formation $\Delta S_i^{F,\Theta}$
3. Solid heat capacity $c_{p,i}^s$

gSAFT for solid/liquid equilibrium

Method 2 (required)

5-18

Molecular Formula	Name
HRb	Rubidium hydride
HS	Mercapto
H ₂ Si	Silylidyne
HTa ₂	Tantalum hydride
H ₂	Hydrogen
H ₂ KN	Potassium amide
H ₂ KO ₄ P	Potassium dihydrogen phosphate
H ₂ LiN	Lithium amide
H ₂ Mg	Magnesium hydride
H ₂ MgO ₂	Magnesium hydroxide
H ₂ N	Amidogen
H ₂ NNa	Sodium amide
H ₂ NRb	Rubidium amide
H ₂ N ₂ O ₂	Nitramide
H ₂ NiO ₂	Nickel(II) hydroxide
H ₂ O	Water
H ₂ O ₂	Hydrogen peroxide
H ₂ O ₂ Sn	Tin(II) hydroxide
H ₂ O ₂ Sr	Strontium hydroxide
H ₂ O ₂ Zn	Zinc hydroxide
H ₂ O ₂ Si	Metasilicic acid
H ₂ O ₂ S	Sulfuric acid
H ₂ O ₂ Se	Selenic acid
H ₂ S	Hydrogen sulfide
H ₂ S ₂	Hydrogen disulfide
H ₂ Se	Hydrogen selenide
H ₂ Sr	Strontium hydride
H ₂ Te	Hydrogen telluride
H ₂ Th	Thorium hydride
H ₂ Zr	Zirconium(II) hydride
H ₂ SiI	Iodosilane
H ₂ N	Ammonia
H ₂ NO	Hydroxylamine
H ₂ O ₂ P	Phosphinic acid
H ₂ O ₂ P	Phosphonic acid
H ₂ O ₂ P	Phosphoric acid
H ₂ P	Phosphine
H ₂ Sb	Stibine

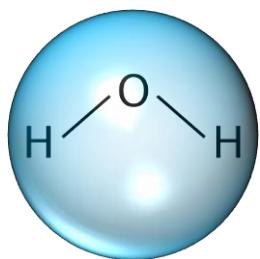
Molecular Formula	Name	ρ_{liq} g/Kg
HRb	Rubidium hydride	32.3
HS	Mercapto	28.8
H ₂ Si	Silylidyne	
HTa ₂	Tantalum hydride	33.9
H ₂	Hydrogen	
H ₂ KN	Potassium amide	33.6
H ₂ KO ₄ P	Potassium dihydrogen phosphate	43.1
H ₂ LiN	Lithium amide	
H ₂ Mg	Magnesium hydride	
H ₂ MgO ₂	Magnesium hydroxide	34.2
H ₂ N	Amidogen	51.5
H ₂ NNa	Sodium amide	
H ₂ NRb	Rubidium amide	
<hr/>		
		-964.4
		-1284.4
		-1124.3
		110.5
		106.1
		-127.7
		-1123.6
		150.8
		145.0
		5.4
		13.5
		210.2
		37.1
		145.1
		147.8
		232.8
		41.1

STANDARD THERMODYNAMIC PROPERTIES OF SUBSTANCE

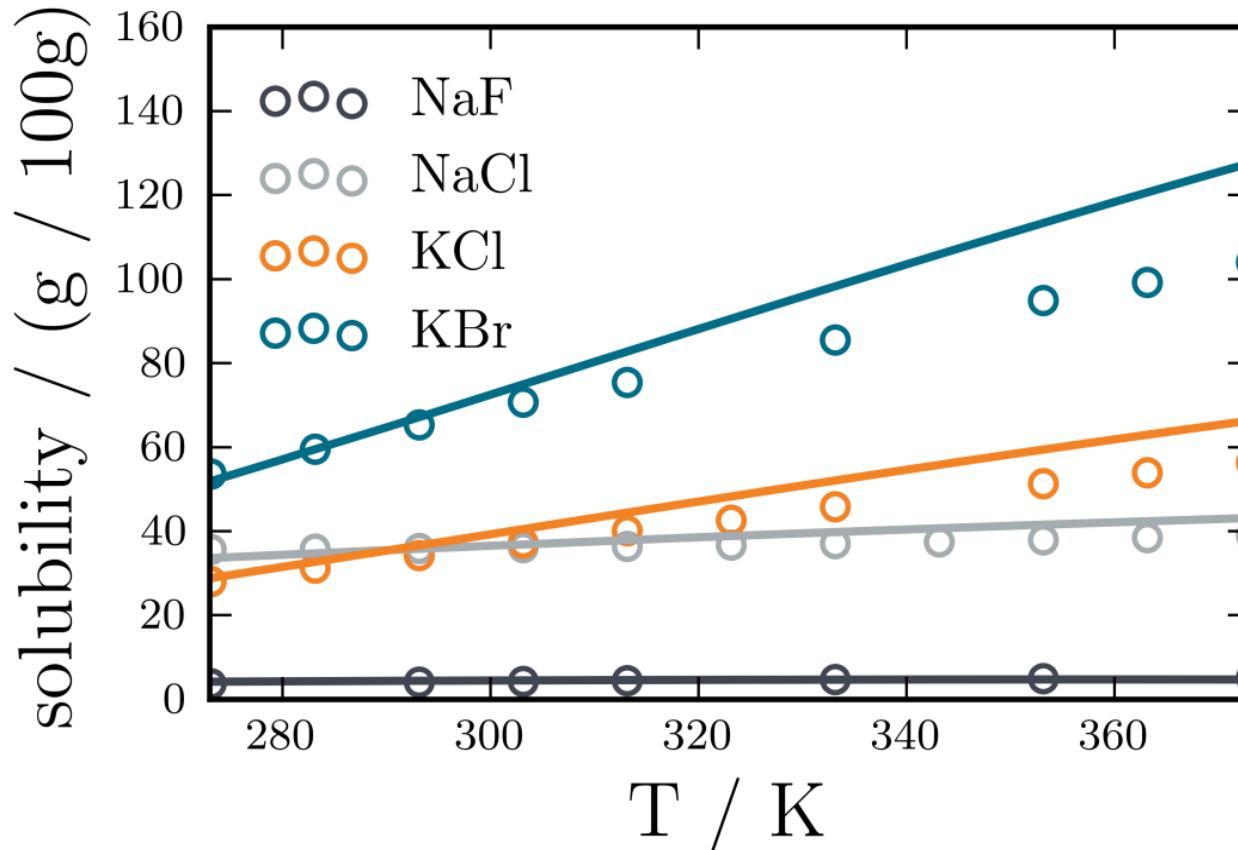
Available for a
organic)

gSAFT for solid/liquid equilibrium

Method 2 (required data: $\Delta_F H^\ominus$; $\Delta_F S^\ominus$; C_p)



Various salts



- Solid-liquid equilibrium condition:

$$\mu_i^s(T, P) = \mu_i^l(T, P, x)$$

Solid phase:

Requires readily available experimental data

Liquid phase:

Predicted with gSAFT

- Solid phase chemical potential – method #3:

- use *empirical* formula

$$\mu_i^s(T) = a + bT$$

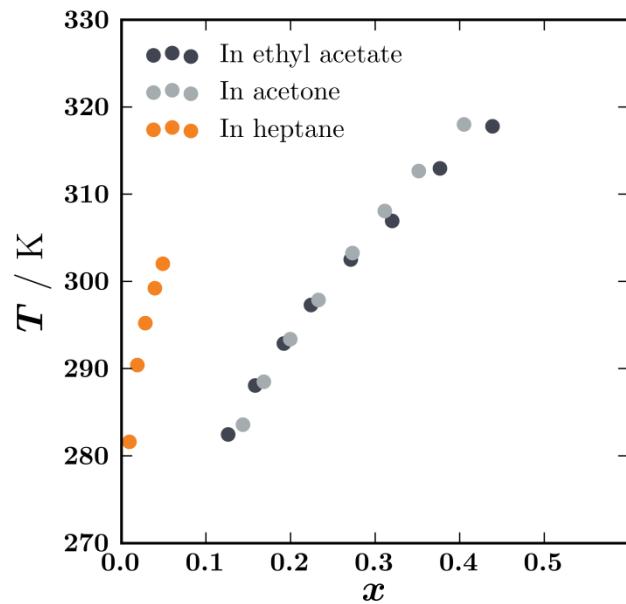
- linear approximation often sufficiently accurate
 - coefficients a, b determined using available solubility data **for any solvent(s)**
 - solid-phase potential is property of solute, independent of the solvent
 - ➔ transferability of solid-phase information across solvents

gSAFT for solid/liquid equilibrium

Method 3 (required data: solubility in any solvent)

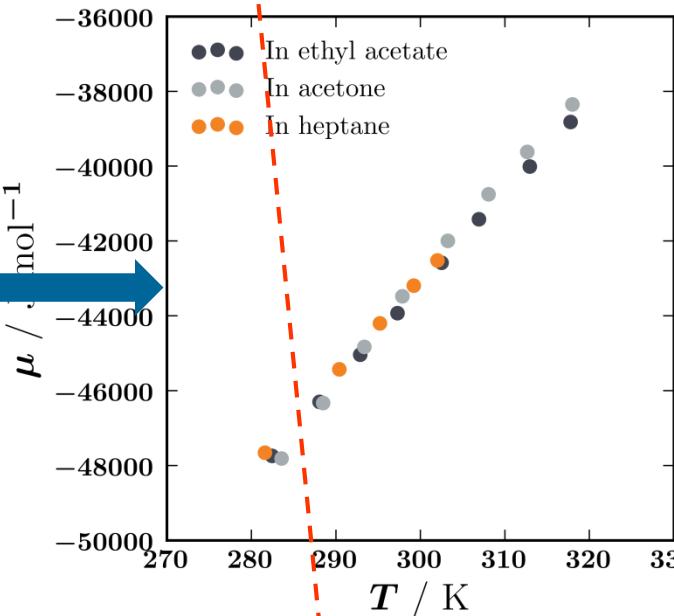
■ Example workflow for ibuprofen:

Step 1: Evaluate the liquid chemical potential of ibuprofen at each experimental solubility point

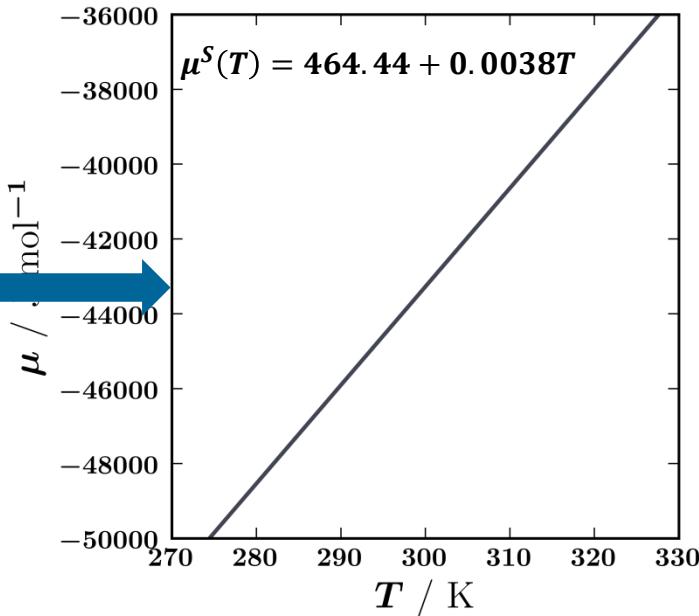


Solubility of Ibuprofen in various solvents

Step 2: Estimate coefficients a, b



Solid-phase chemical potential of Ibuprofen at various temperatures



“Universal” chemical potential of Ibuprofen solid

gSAFT for solid/liquid equilibrium

Method 3 (required data: solubility data in any solvent)



- Example workflow for ibuprofen:

$$\mu^S(T) = 464.44 + 0.0038T$$

$$\mu^S(T) = 464.44 + 0.0038T$$

- Solid-phase chemical potential for ibuprofen
- Universally applicable to determine solubility in *any* solvent mixture

gSAFT for reactive systems



Equilibrium in single-phase systems

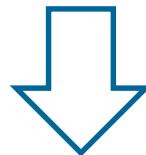
Single-phase system
@
uniform T, P

Equilibrium: minimise free energy of system

$$G(T, P, \mathbf{n}) = \sum_{i=1}^{NC} n_i \mu_i(T, P, \mathbf{n})$$

...subject to **specified** set of chemical reactions

$$n_i = n_i^o + \sum_{j=1}^{NR} v_{ij} \xi_j, \quad \forall i = 1, \dots, NC$$



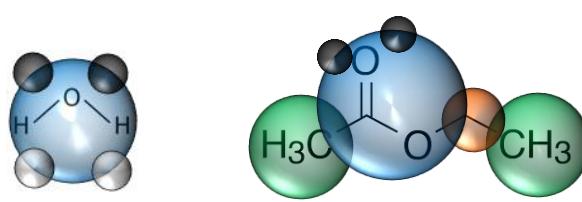
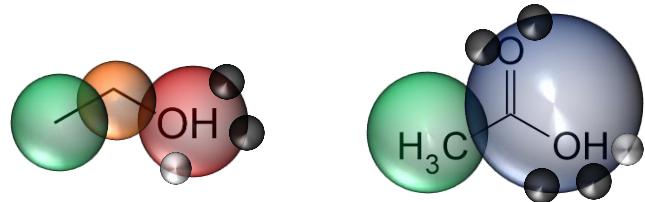
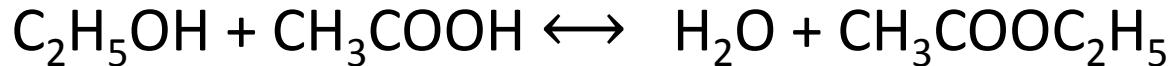
Fundamental equilibrium condition

$$\sum_{i=1}^{NC} v_{ij} \mu_i(T, P, \mathbf{n}) = 0, \quad \forall j = 1, \dots, NR$$

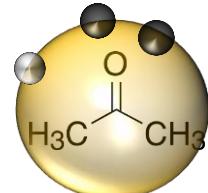
Esterification reaction

gSAFT predictions at T = 313.15 K

Esterification reaction in acetone:



Solvent:

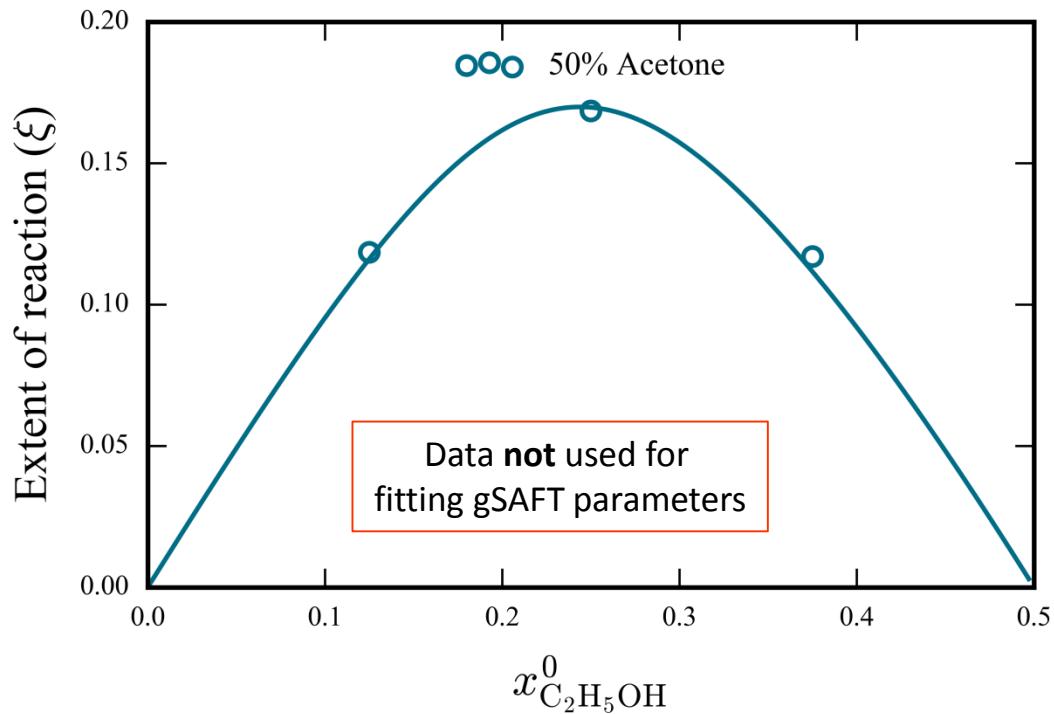


Initial mixture (mol/mol)

- Acetone : 0.5
- Ethanol : x^o
- Acetic acid : $0.5 - x^o$



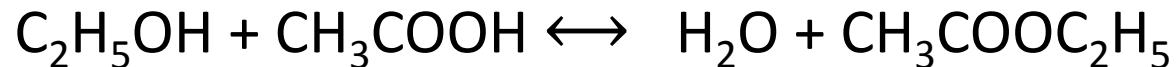
Accurate predictions for
all input compositions



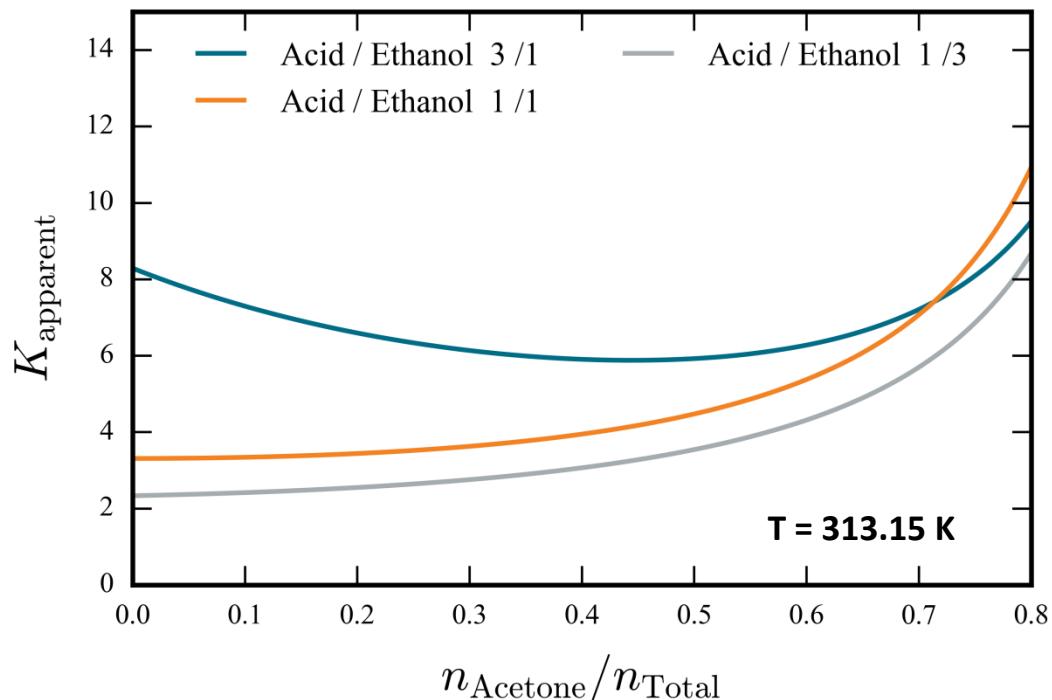
Esterification reaction

A look at the apparent equilibrium constant...

Esterification reaction in acetone:



$$K_{apparent} = \frac{[H_2O][CH_3COOC_2H_5]}{[C_2H_5OH][CH_3COOH]}$$



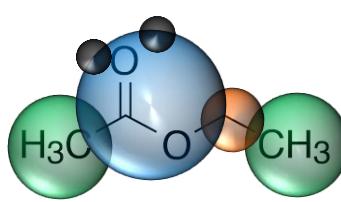
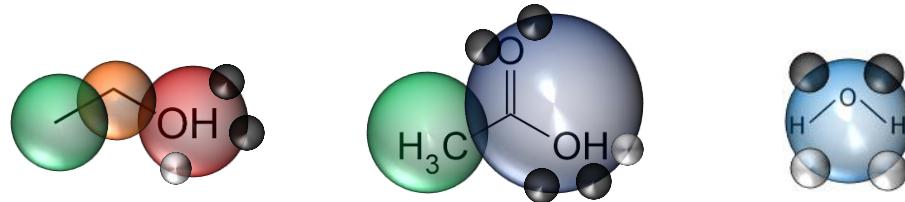
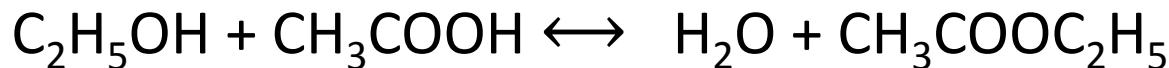
Strong dependence on initial composition!

Using apparent equilibrium “constants” is **not** a predictive methodology...

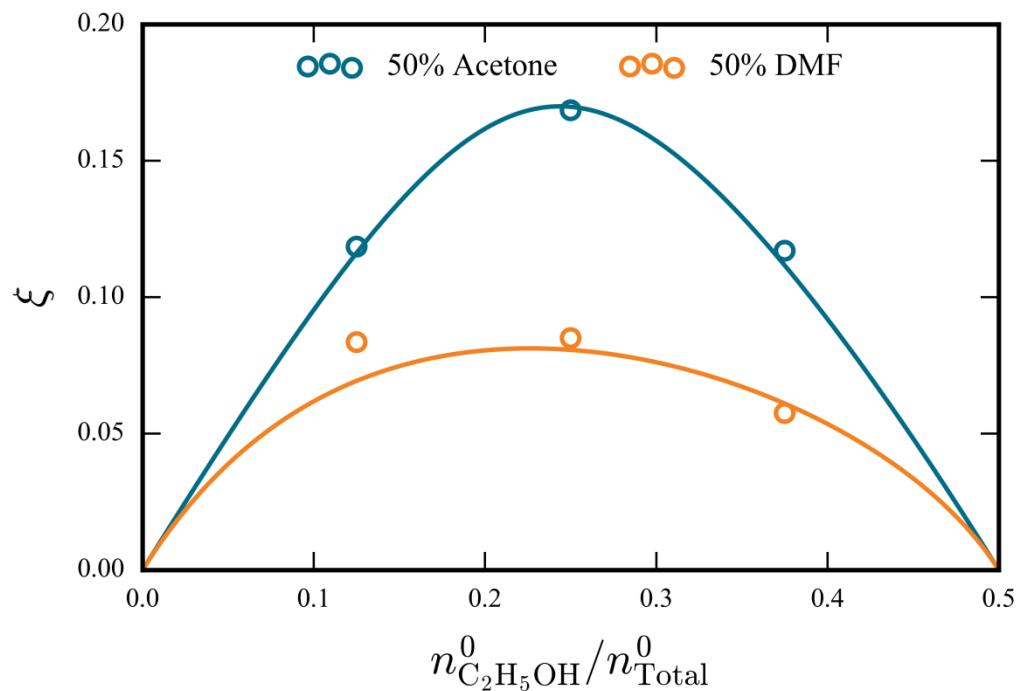
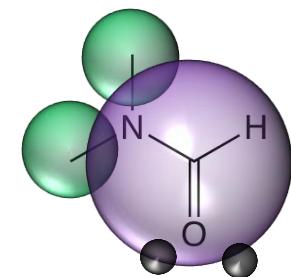
Esterification reaction

Influence of changing the solvent: gSAFT predictions

Esterification reaction in DMF:



Solvent:



Replacing acetone by DMF leads to significant decrease in reaction extent

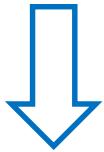
A purely thermodynamic phenomenon:
intermolecular interactions with DMF
decrease activity of reactants,
increase activity of products
→ shift equilibrium to the left!

Computing the true* equilibrium constants

*composition-independent



Fundamental equilibrium condition



$$\sum_{i=1}^{NC} \nu_{ij} \mu_i = 0$$

Reformulations based on equilibrium “constants”

Using fugacities

$$K(T) = \prod_{i=1}^{NC} (f_i(T, P, \mathbf{n}) / P^\ominus)^{\nu_i}$$

where

$$K(T) \equiv \exp \left(-\frac{\sum_{i=1}^{NC} \nu_i \Delta g_i^F(T, P^\ominus)}{RT} \right)$$

Using symmetric activities

$$K'(T, P) = \prod_{i=1}^{NC} (a_i(T, P, \mathbf{n}))^{\nu_i}$$

where

$$K'(T, P) \equiv \exp \left(-\frac{\sum_{i=1}^{NC} \nu_i \mu_i^o(T, P)}{RT} \right)$$

Using asymmetric activities

(several definitions depending on composition scale)

$$K''(T, P) = \prod_{i=1}^{NC} (\tilde{a}_i(T, P, \mathbf{n}))^{\nu_i}$$

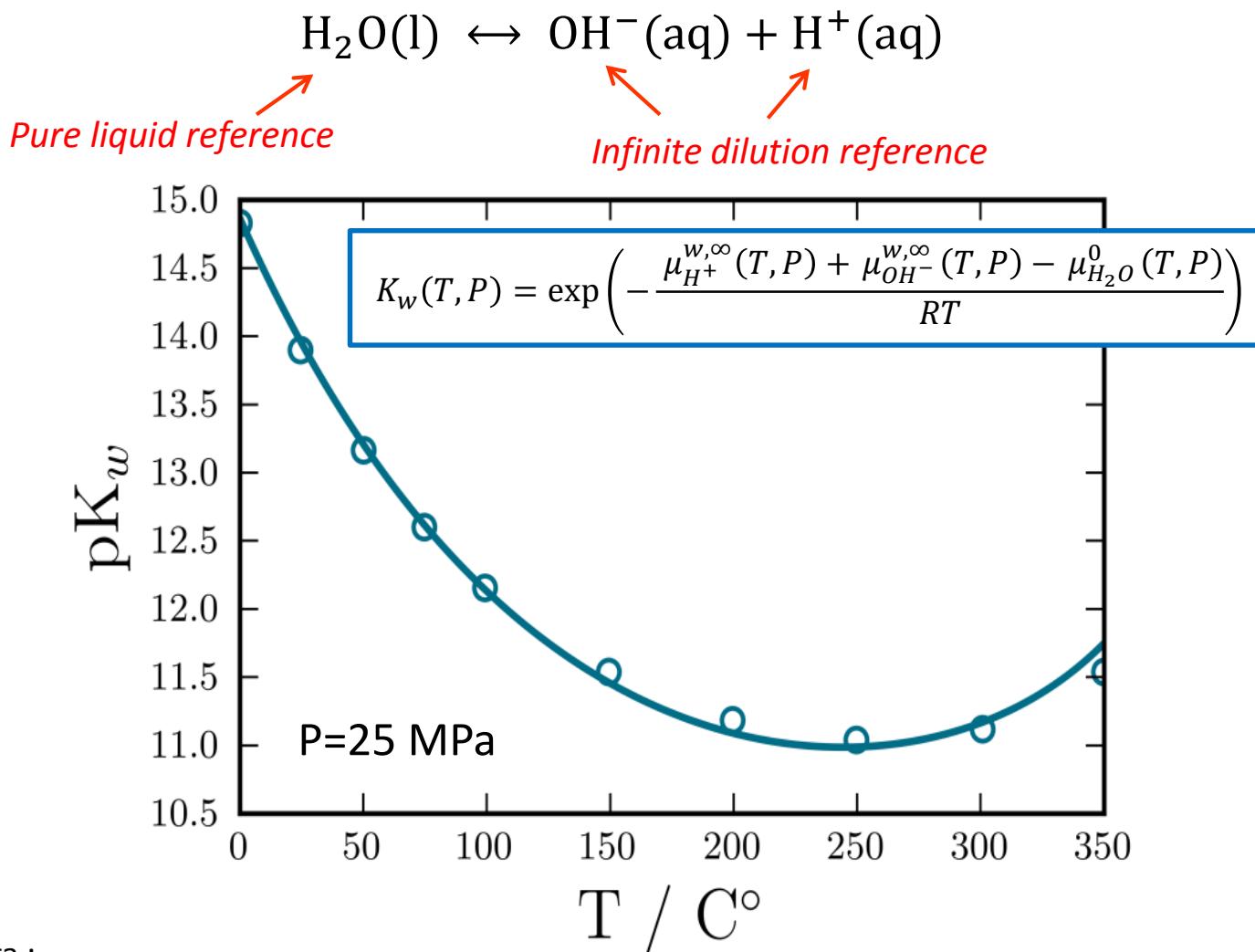
where

$$K''(T, P) \equiv \exp \left(-\frac{\sum_{i=1}^{NC} \nu_i \mu_i^{w,\infty}(T, P)}{RT} \right)$$

→ Equilibrium constant for a reaction is **not** unique
Depends on choice of reference state

Computing the true equilibrium constants

Example: dissociation constant of water



Experimental data :

International Association for the Properties of Water and Steam (IAPWS)

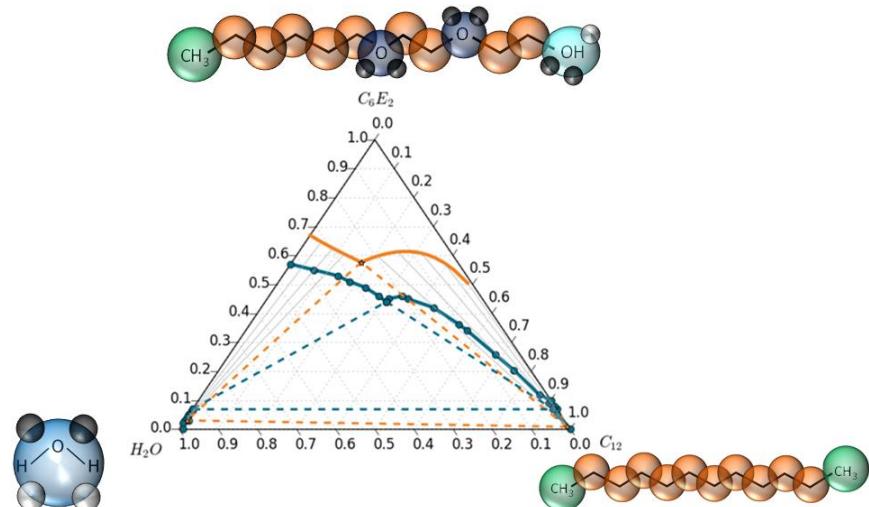
Conclusions



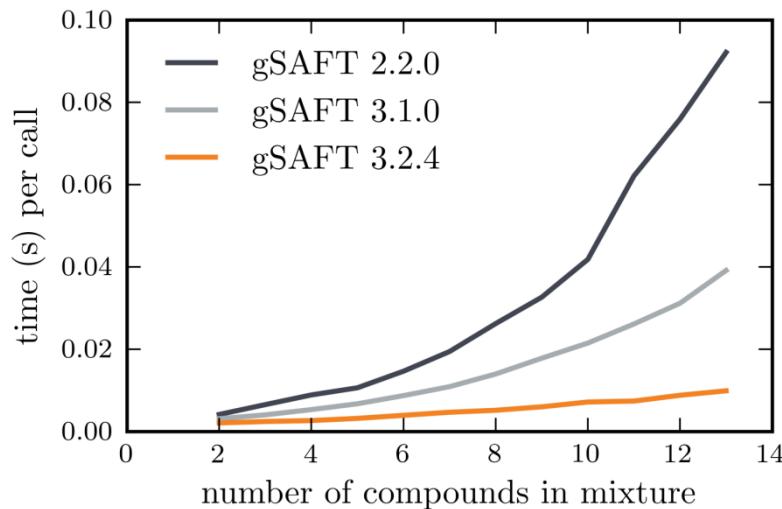
Conclusions on gSAFT – I

Powerful predictive thermodynamic modelling within gPROMS

- State-of-the-art group contribution approach
→ **predictive accuracy**



- Major enhancements in computational efficiency
→ **practically applicable to wide range of systems**



Conclusions on gSAFT – II

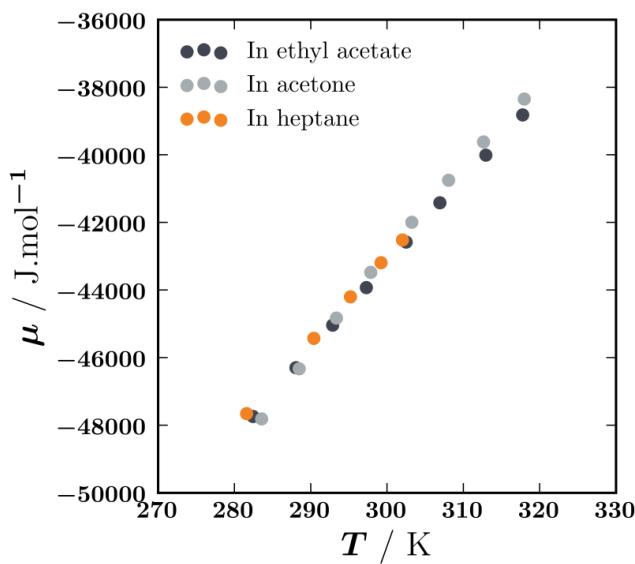
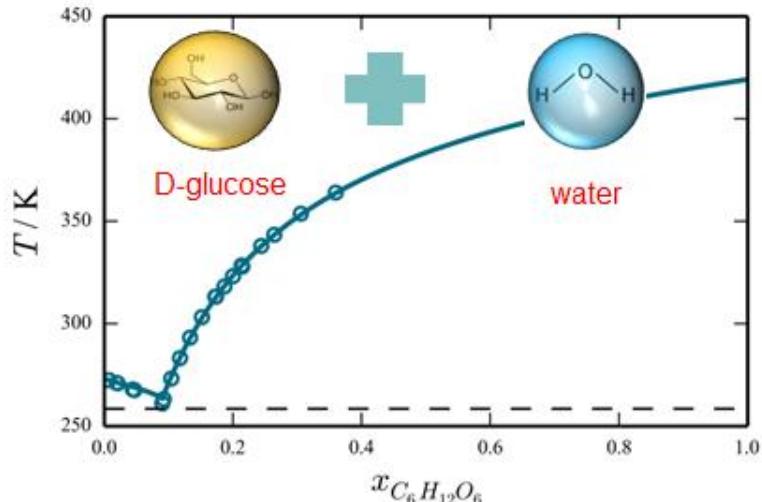
Accurate modelling of systems with solid phases

- 3 different approaches for computation of solid-phase potential

- based on readily available experimental data

- Theoretically rigorous way of achieving transferability of information from experimental solubility data across different solvents

- takes advantage of gSAFT's accurate representation of liquid phases to characterise solid-phase potentials

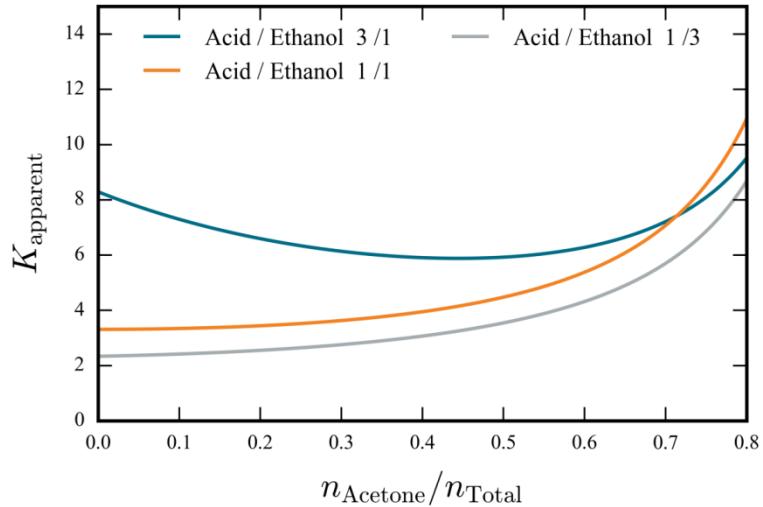
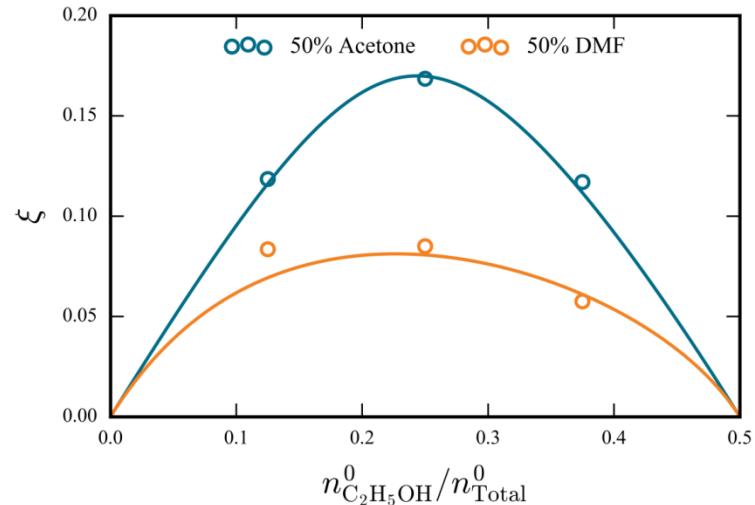


Conclusions on gSAFT – III

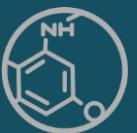
Accurate modelling of systems with reaction equilibrium

- gSAFT offers predictive accuracy for reactive systems
 - based on correct mathematical formulation of equilibrium conditions

- Commonly used apparent equilibrium “constants” are of limited applicability

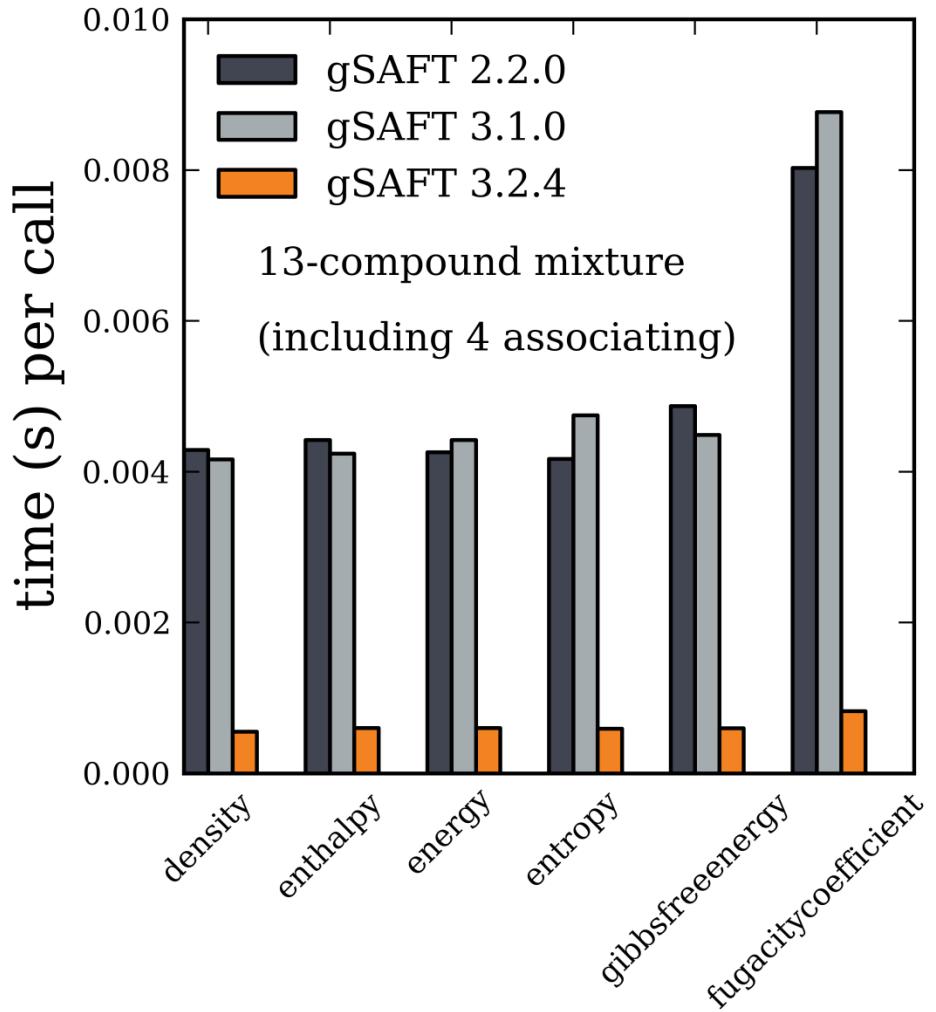
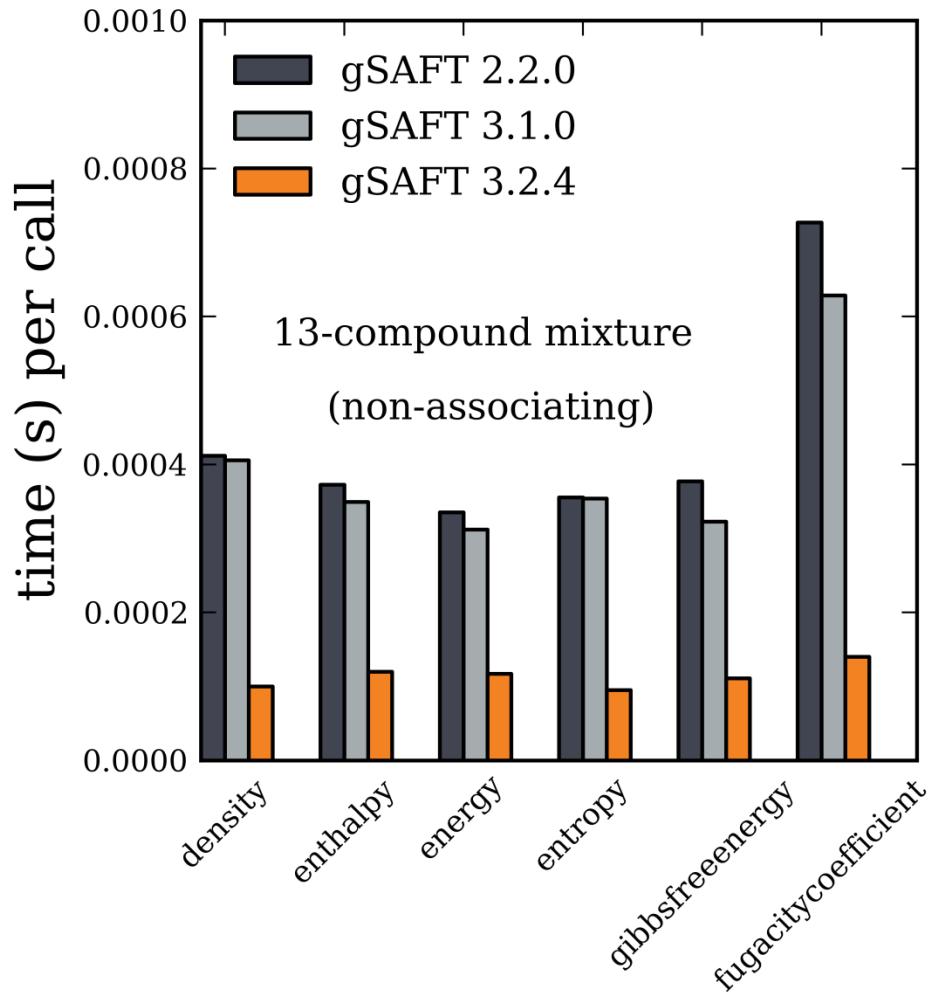


Thank you



Performance improvements - II

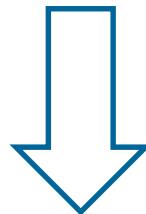
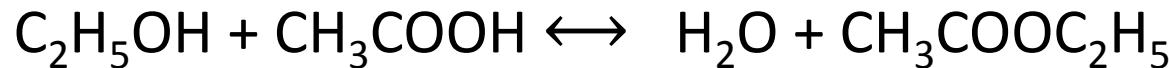
Single phase properties – absolute times



Esterification reaction

Fundamental equations

Esterification reaction **in acetone**:



$$\min_{\xi, \mathbf{n}} G(T, P, \mathbf{n})$$

All chemical potentials need to be computed from the same **element** reference state !

Fundamental equilibrium condition:

$$-\mu_{\text{C}_2\text{H}_5\text{OH}} - \mu_{\text{CH}_3\text{COOH}} + \mu_{\text{H}_2\text{O}} + \mu_{\text{CH}_3\text{COOC}_2\text{H}_5} = 0$$

Material Constraints:

$$n_{\text{C}_2\text{H}_5\text{OH}} = n_{\text{C}_2\text{H}_5\text{OH}}^0 - \xi$$

$$n_{\text{CH}_3\text{COOH}} = n_{\text{CH}_3\text{COOH}}^0 - \xi$$

$$n_{\text{H}_2\text{O}} = n_{\text{H}_2\text{O}}^0 + \xi$$

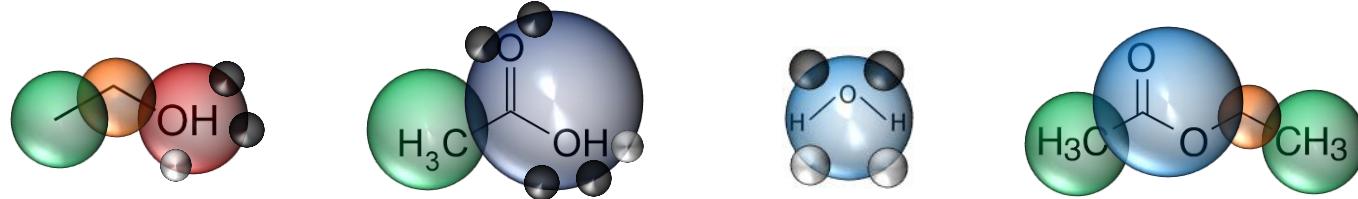
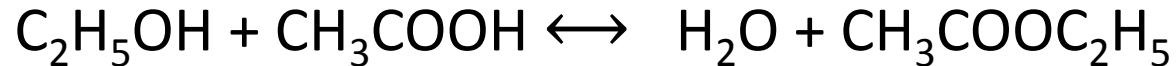
$$n_{\text{CH}_3\text{COOC}_2\text{H}_5} = n_{\text{CH}_3\text{COOC}_2\text{H}_5}^0 + \xi$$

→No need for the knowledge of the so-called equilibrium constants!

Esterification reaction

gSAFT predictions at T = 313.15 K

Esterification reaction **in acetone**:



Initial state:

$$n_{\text{C}_2\text{H}_5\text{OH}}^0$$

$$n_{\text{CH}_3\text{COOH}}^0$$

$$n_{\text{H}_2\text{O}}^0 = 0$$

$$n_{\text{CH}_3\text{COOC}_2\text{H}_5}^0 = 0$$

Solvent:
 $n_{\text{CH}_3\text{COCH}_3} = 0.5 \text{ mol}$



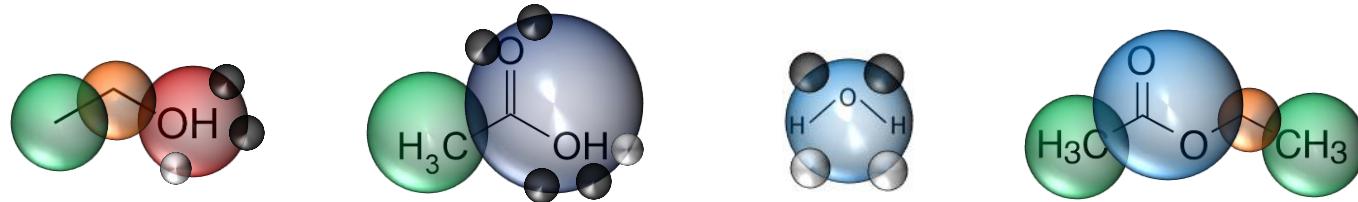
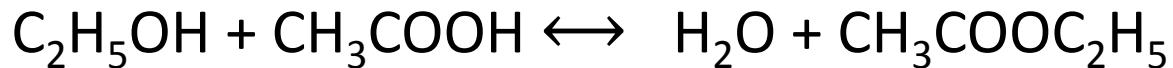
Consider different ratios of ethanol to acetic acid

→ Apply Gibbs free energy minimization using gSAFT

Esterification reaction

Influence of changing the solvent

Esterification reaction in DMF:



Initial state:

$$n_{\text{C}_2\text{H}_5\text{OH}}^0$$

$$n_{\text{CH}_3\text{COOH}}^0$$

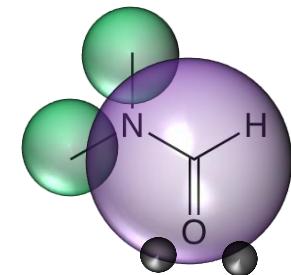
$$n_{\text{H}_2\text{O}}^0 = 0$$

$$n_{\text{CH}_3\text{COOC}_2\text{H}_5}^0 = 0$$



Consider different ratios of ethanol to acetic acid
(now using DMF as the solvent)

Solvent:



$$n_{\text{DMF}} = 0.5 \text{ mol}$$

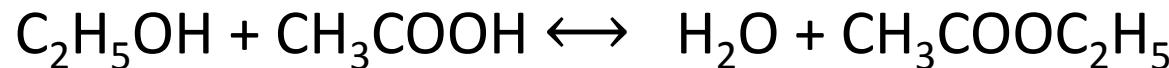
Fundamental equilibrium condition is not changed!

$$-\mu_{\text{C}_2\text{H}_5\text{OH}} - \mu_{\text{CH}_3\text{COOH}} + \mu_{\text{H}_2\text{O}} + \mu_{\text{CH}_3\text{COOC}_2\text{H}_5} = 0$$

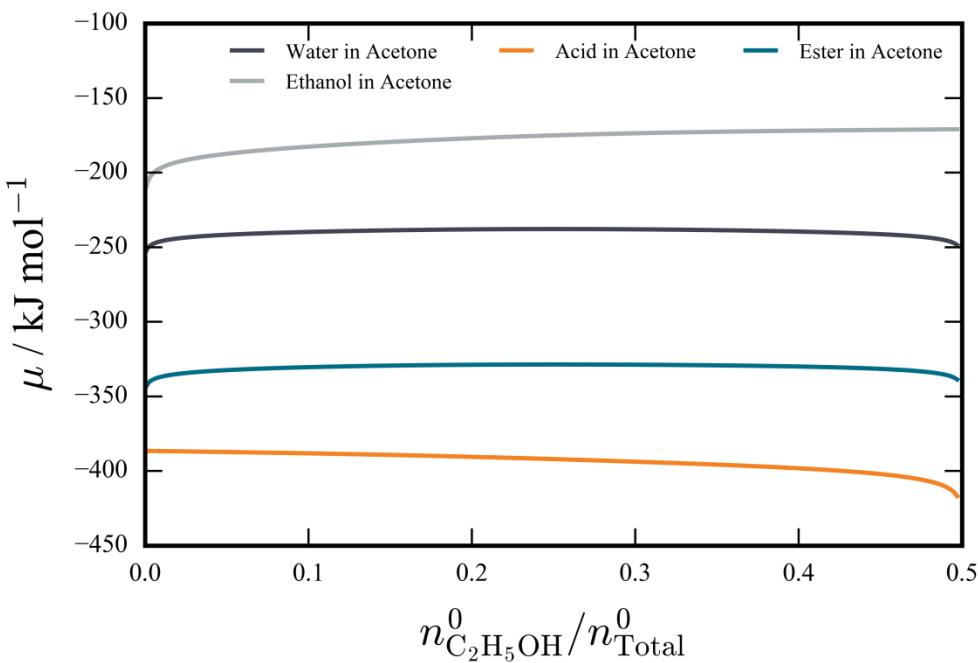
Esterification reaction

Influence of changing the solvent - explanation

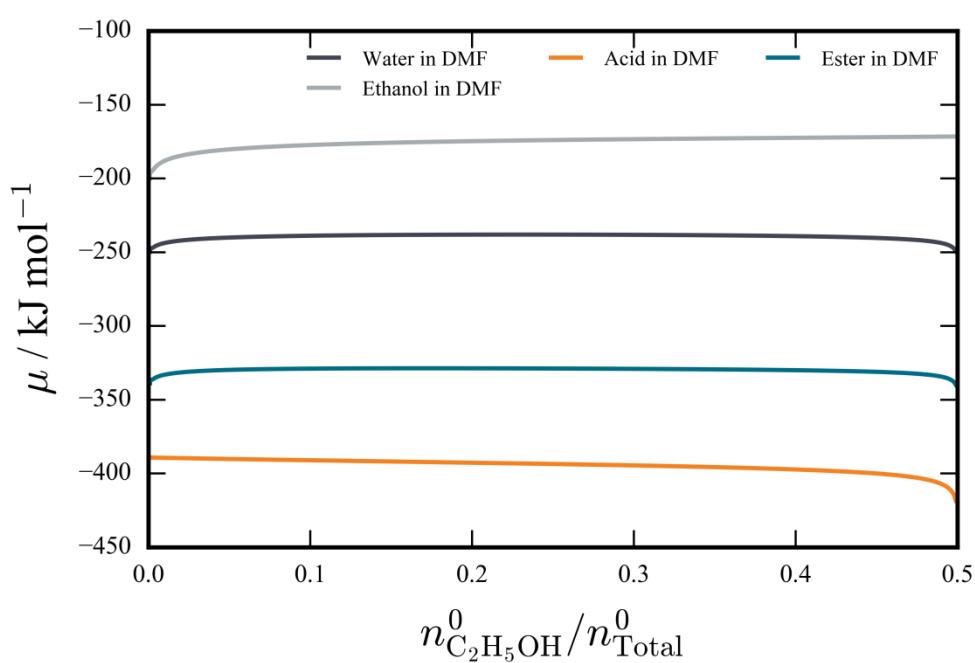
Esterification reaction :



Chemical potentials in acetone



Chemical potentials in DMF

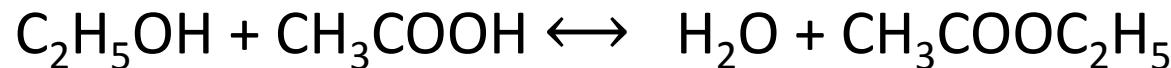


Difference is clearer if we isolate the composition dependence of the chemical potential
→ We need to look at the symmetric activity coefficients

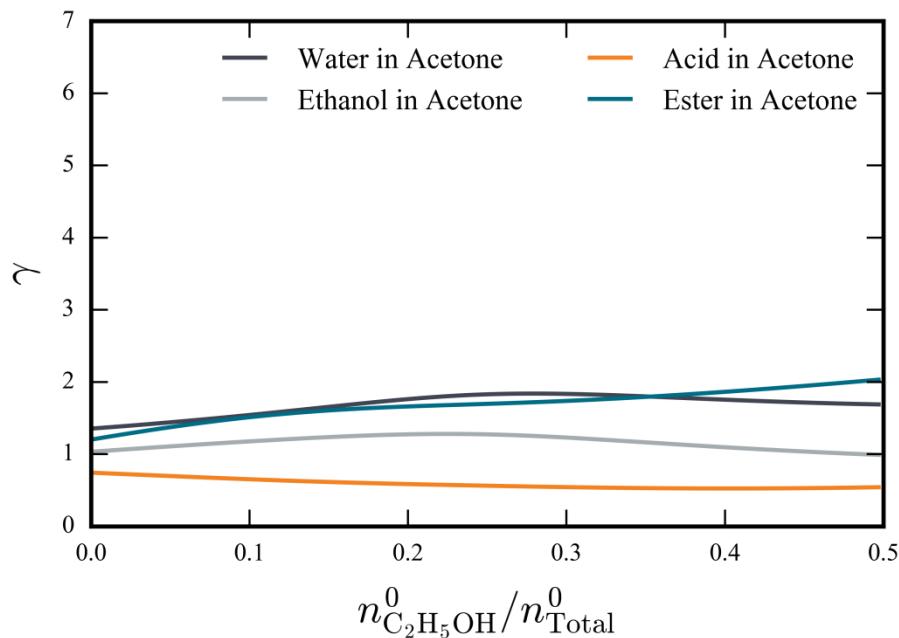
Esterification reaction

Influence of changing the solvent - explanation

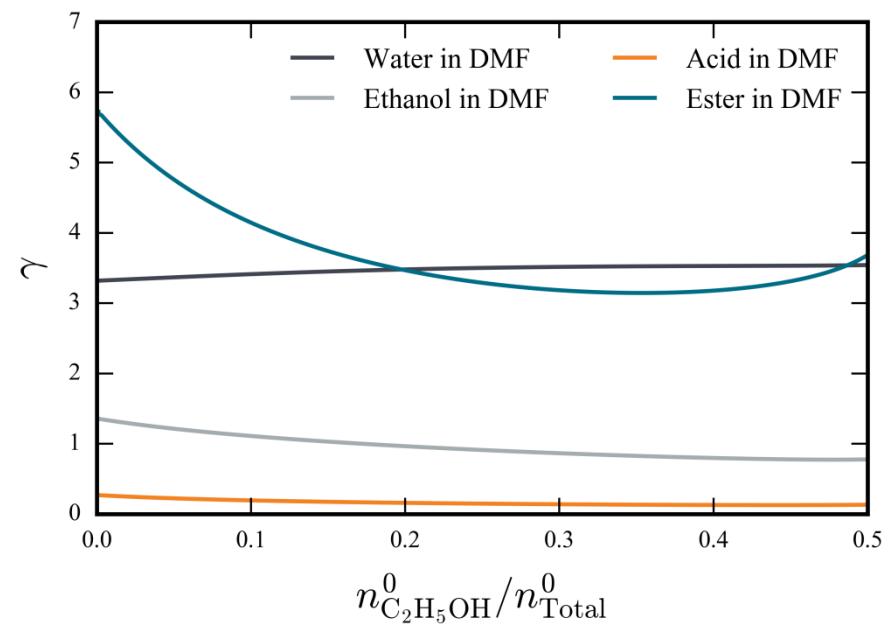
Esterification reaction :



Activity coefficients in acetone



Activity coefficients in DMF



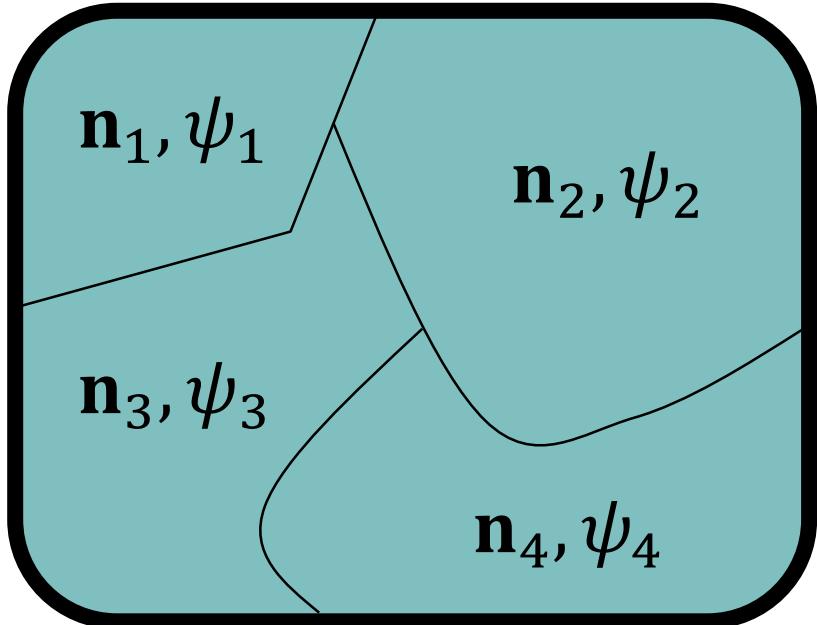
Symmetric activity coefficients strongly affected by the change of solvent !

gSAFT for reactive systems

II – multiphase systems



Multiphase system @ uniform T, P



Free energy of system

$$G = \sum_{k=1}^{NP} \sum_{i=1}^{NC} n_{ik} \left(\mu_i^{[k]} + F \psi_k q_i \right)$$

Chemical potential of species i in phase k

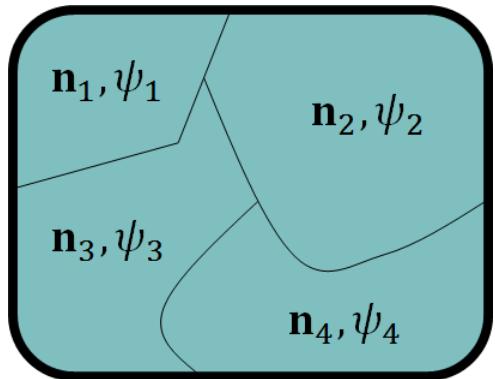
Electrical potential of phase k

amount of species i in phase k

charge of species i

Faraday constant
 $9.64853399 \times 10^4 \text{ C mol}^{-1}$

Equilibrium in multiphase systems



Equilibrium: minimise free energy of system

$$G = \sum_{k=1}^{NP} \sum_{i=1}^{NC} n_{ik} (\mu_i^{[k]} + F \psi_k q_i)$$

subject to ...all “**admissible**” transformations of material

1. **Assume** free exchange of material between phases but no chemical reactions → “Phase Equilibrium”

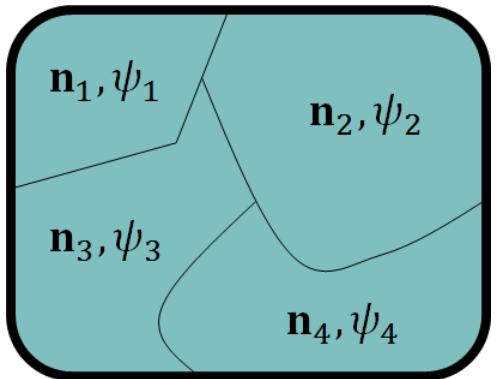
$$\sum_{k=1}^{NP} n_{ik} = n_i^o, \forall i = 1, \dots, NC$$

2. **Assume** free exchange of material between phases and specified set of chemical reactions → “Phase & Reaction Equilibrium”

$$\sum_{k=1}^{NP} n_{ik} = n_i^o + \sum_{j=1}^{NR} v_{ij} \xi_j, \quad \forall i = 1, \dots, NC$$

Equilibrium in multiphase reactive systems

First-order optimality conditions



$$\min_{n_{ik}, \psi_k, \xi_j} G = \sum_{k=1}^{NP} \sum_{i=1}^{NC} n_{ik} (\mu_i^{[k]} + F \psi_k q_i)$$

subject to:

$$\sum_{k=1}^{NP} n_{ik} = n_i^o + \sum_{j=1}^{NR} v_{ij} \xi_j, \quad \forall i = 1, \dots, NC$$

**$NC \times NP + NR$ equations in
 n_{ik}, ξ_j**

“Reaction equilibrium” $\sum_{i=1}^{NC} v_{ij} \mu_i^{[NP]} = 0, \quad \forall j = 1, \dots, NR$

“Phase equilibrium” $\mu_i^{[k]}(T, P, \mathbf{n}_k) = \mu_i^{[NP]}(T, P, \mathbf{n}_k), \quad \forall i \in \mathcal{N}$

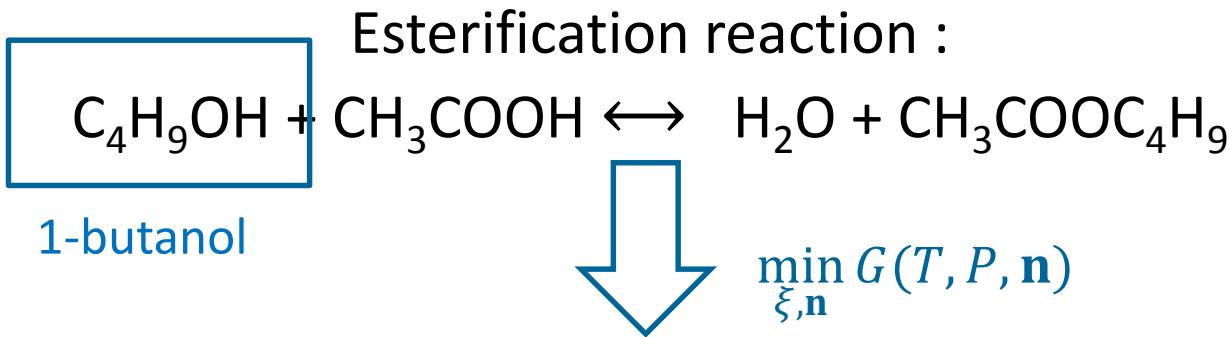
“!!??!!”
$$\frac{\mu_i^{[k]}(T, P, \mathbf{n}_k) - \mu_i^{[NP]}(T, P, \mathbf{n}_{NP})}{q_i} = \frac{\mu_{i'}^{[k]}(T, P, \mathbf{n}_k) - \mu_{i'}^{[NP]}(T, P, \mathbf{n}_{NP})}{q_{i'}}, \forall i, i' \in \mathcal{C} \quad \left. \right\} k = 1, \dots, NP - 1$$

“Electroneutrality” $\sum_{i=1}^{NC} q_i n_{ik} = 0$

Neutral species ($q_i = 0$)
Charged species ($q_i \neq 0$)

Esterification reaction

With multiple phases at equilibrium



Reaction equilibrium:

$$-\mu_{\text{C}_4\text{H}_9\text{OH}} - \mu_{\text{CH}_3\text{COOH}} + \mu_{\text{H}_2\text{O}} + \mu_{\text{CH}_3\text{COOC}_4\text{H}_9} = 0$$

Phase equilibrium:

$$\mu_i^{[k]} = \mu_i^{[NP]} \quad \forall i \in \mathcal{N}$$

Material Constraints:

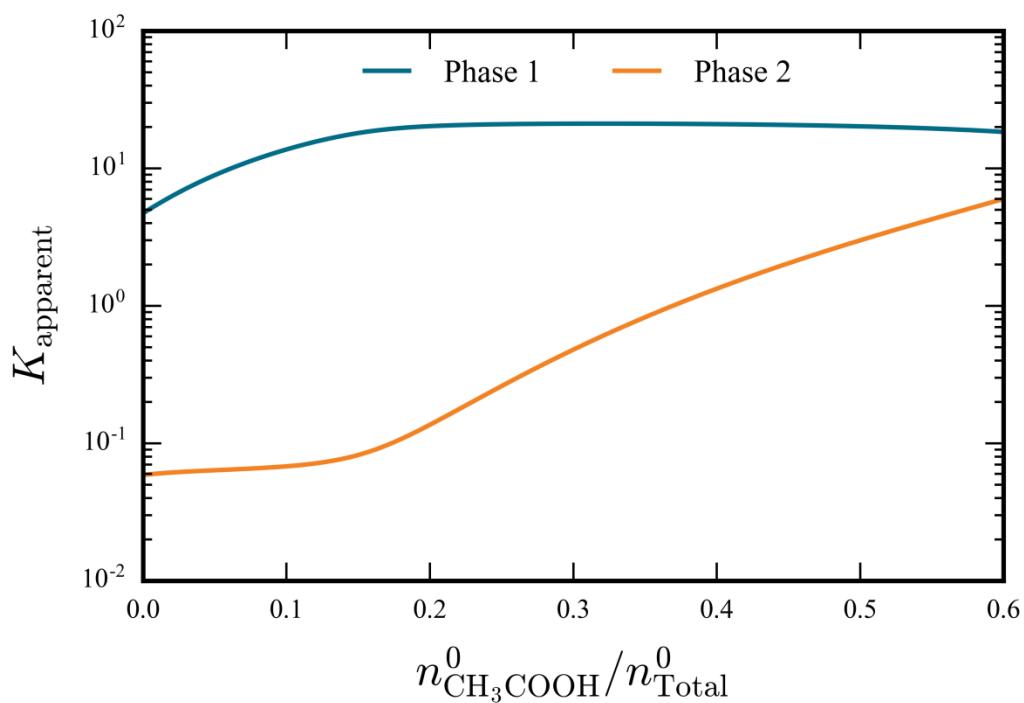
$$\begin{aligned} n_{\text{C}_4\text{H}_9\text{OH}} &= n_{\text{C}_4\text{H}_9\text{OH}}^0 - \xi \\ n_{\text{CH}_3\text{COOH}} &= n_{\text{CH}_3\text{COOH}}^0 - \xi \\ n_{\text{H}_2\text{O}} &= n_{\text{H}_2\text{O}}^0 + \xi \\ n_{\text{CH}_3\text{COOC}_4\text{H}_9} &= n_{\text{CH}_3\text{COOC}_4\text{H}_9}^0 + \xi \end{aligned}$$

LLE is found at global minimum of Gibbs free energy

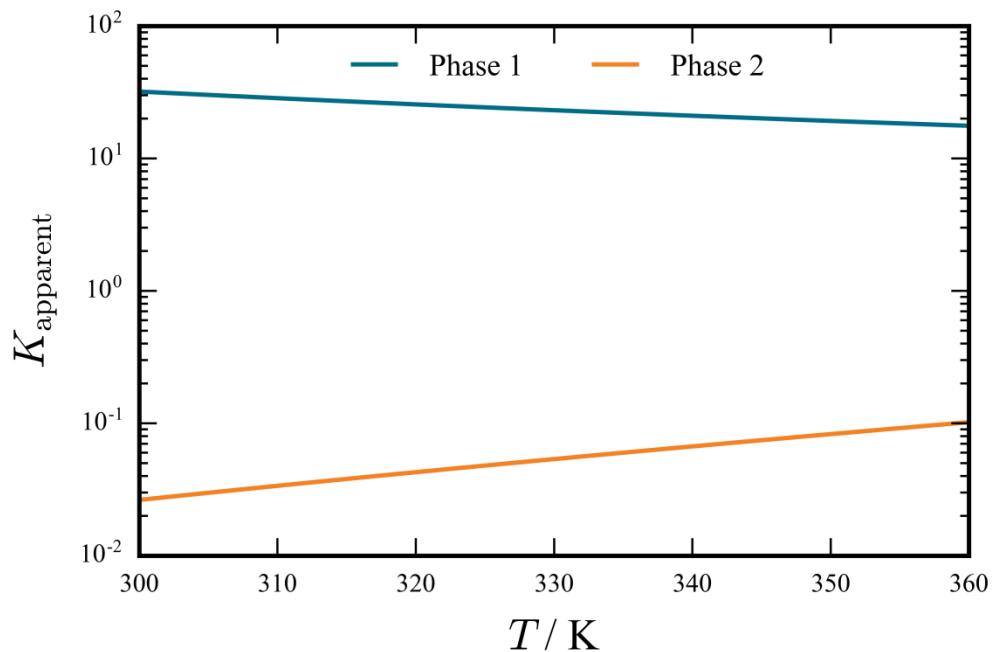
Esterification reaction

Another look at the apparent equilibrium constant...

Variation with input composition



Variation with temperature



Apparent equilibrium constants are **useless** in this context...

■ gSAFT: powerful thermodynamic modelling within gPROMS

- State-of-the-art group contribution approach → predictive accuracy
- Major enhancements in computational efficiency
→ practically applicable to wide range of applications

■ Modelling of systems with solid phase(s)

- 3 different approaches for computation of solid-phase potential
 - based on readily available experimental data
- Theoretically rigorous way of achieving transferability of information from experimental solubility data across different solvents
 - takes advantage of gSAFT's accurate representation of liquid phases to characterise solid-phase potentials

■ Modelling of systems with reaction equilibrium

- gSAFT offers predictive accuracy based on correct mathematical formulation
- **Commonly used apparent equilibrium “constants” are of limited applicability**