Sustainable mobility | New energies | Responsible oil and gas

Ele-Ther:

e-Thermodynamics Joint Industrial Project (JIP)

An Industrial Community on Electrolyte Thermodynamics

User community

Energies nouvelles

Software community

NESTE

BASF We create chemistry

BAYER

orano

covestro

SOLVAY

aspentech

Hafnium Labs

ProSim

ELECTROLYTE THERMODYNAMICS
REACTIVE SYSTEMS WITH MIXED SOLVENTS

Industrial & Technical context

- New processes involve electrolytic systems including ionic species and chemical reactions
  - Transformation of biomass
  - Battery
  - CO_2 capture
  - Geothermal context
  - Metal purification and recycling
  - ….

- Need of methodologies and benchmark of process solutions
  ➔ proposal of the JIP Elether2

Need for
- Reaction constants
- Non-ideality model
- Algorithm to compute equilibrium

Apparent species differ from true species
⇒ Parameterization involves many more compounds
⇒ identify best practices
⇒ Promote collaborative work

AIM OF THE JIP

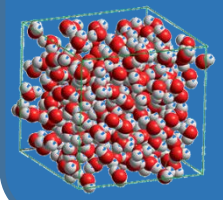
- Create **a peer network** in the industrial (and later academic) community to promote work on Electrolyte Thermodynamics
- Develop **best practices** for the workflow :

Data collection

➔From Detherm **database** & **textbooks**

➔First analysis: **check data consistency**

Advanced tools for validation & extrapolation



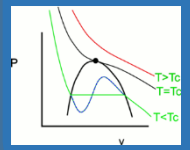
➔Use statistical models

- **molecular simulation**
- **SAFT equation of state**
- **…**

➔extrapolate T/P/salinity range

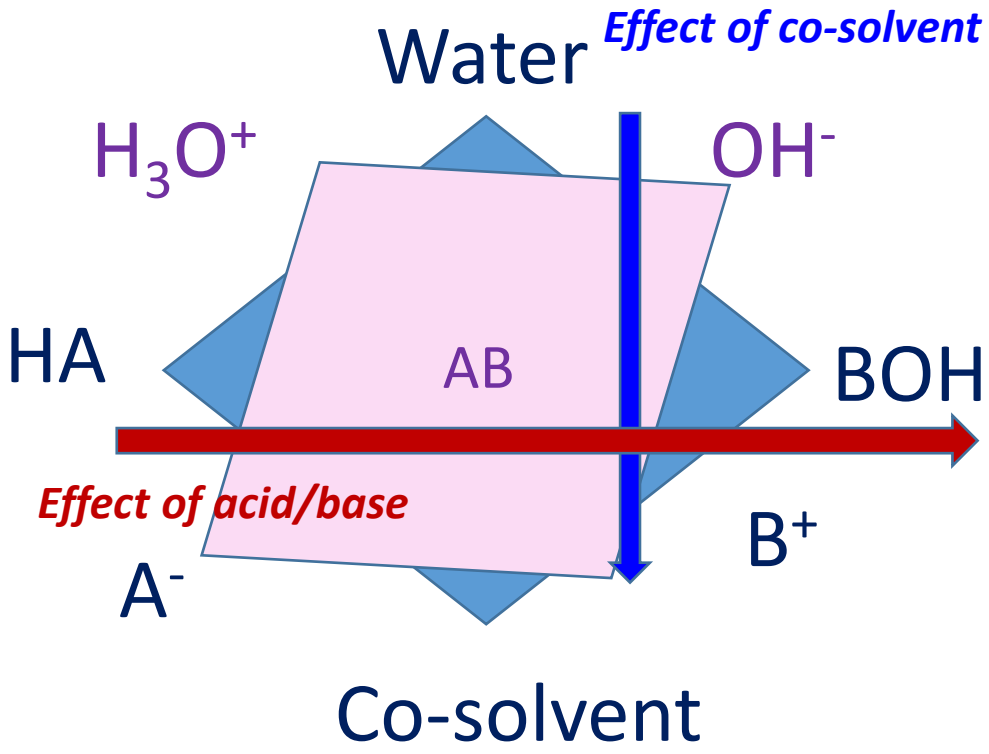
➔ identify limits where new data are needed

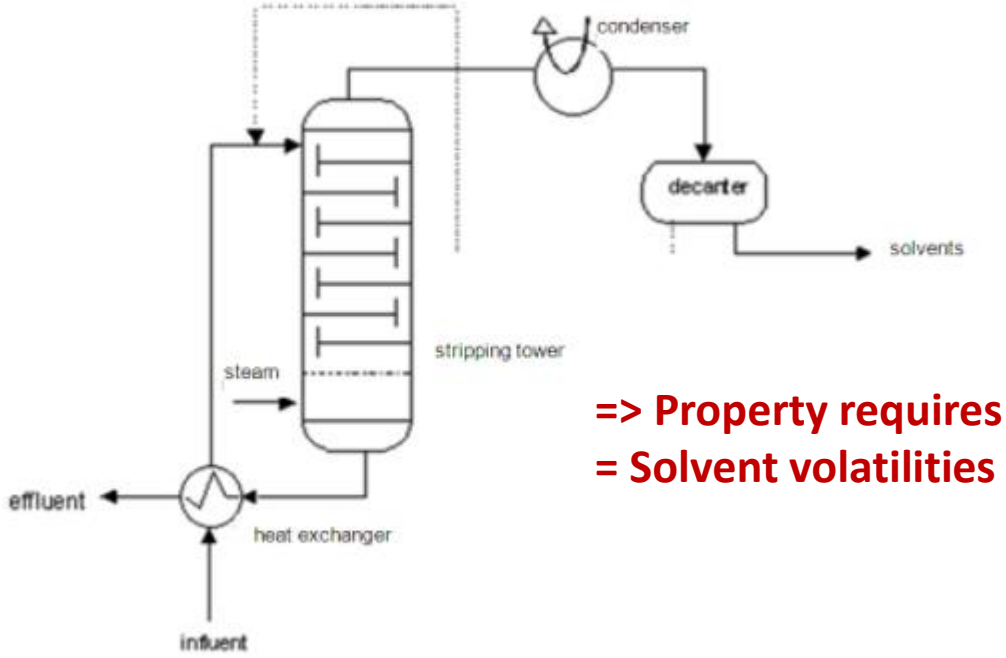
Correlative models calibration



➔Use experimental data and « pseudo-experimental » data to **calibrate** an industrial model (**correlative model**)

CASE STUDY ANALYSIS





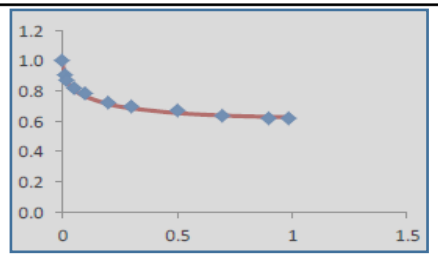
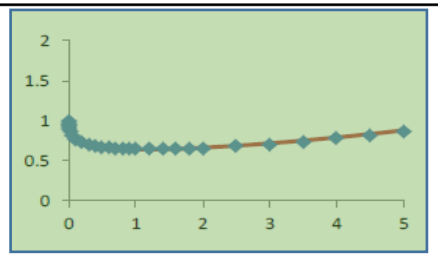
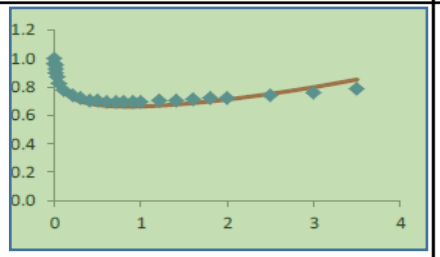
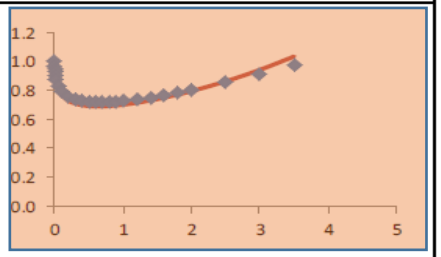
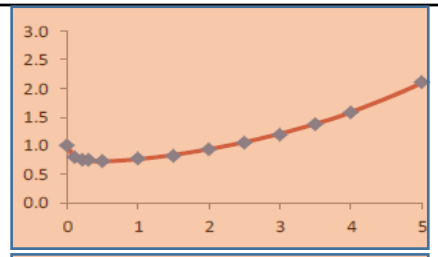
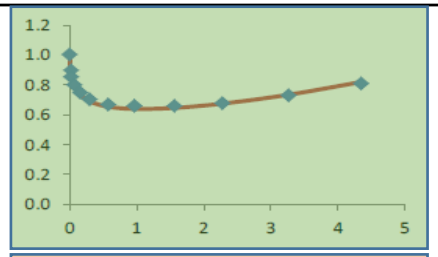
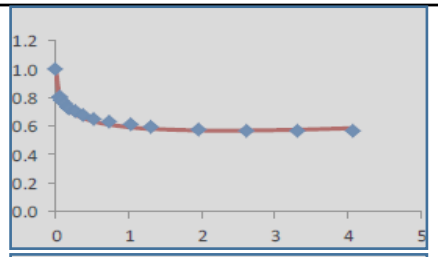
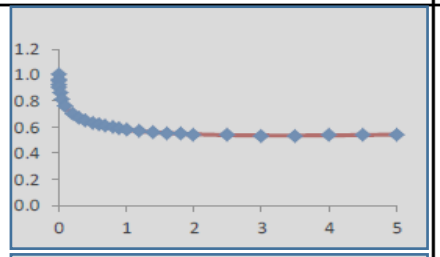
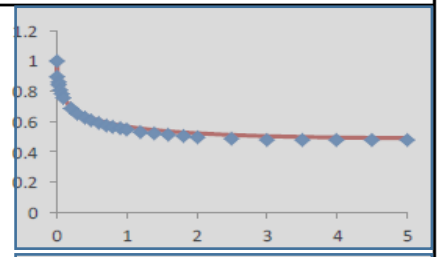
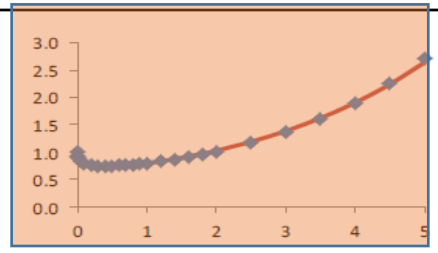
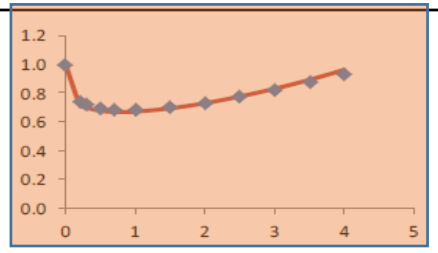
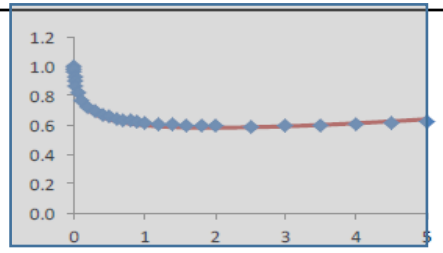
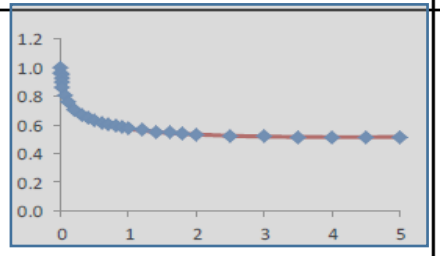
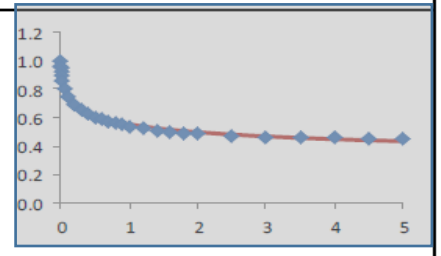
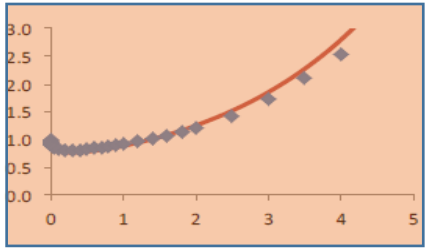
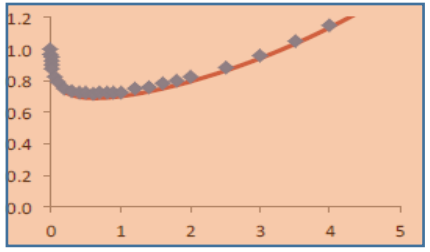
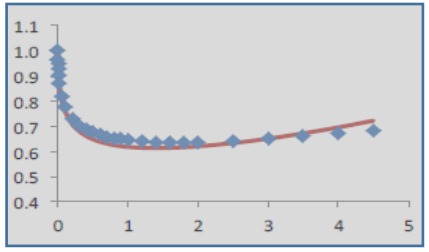
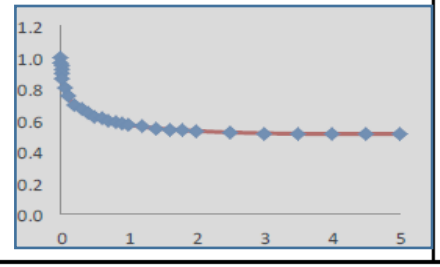
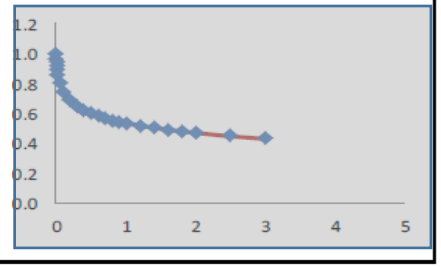
=> Property requires
= Solvent volatilities

OUTLINE

- Introduction
- Water + salt
- Mixed solvent + salt
- Quaternary analysis
- Parameterization of a ternary system
- Back to some fundamentals: how to improve predictivity
- Conclude / perspectives

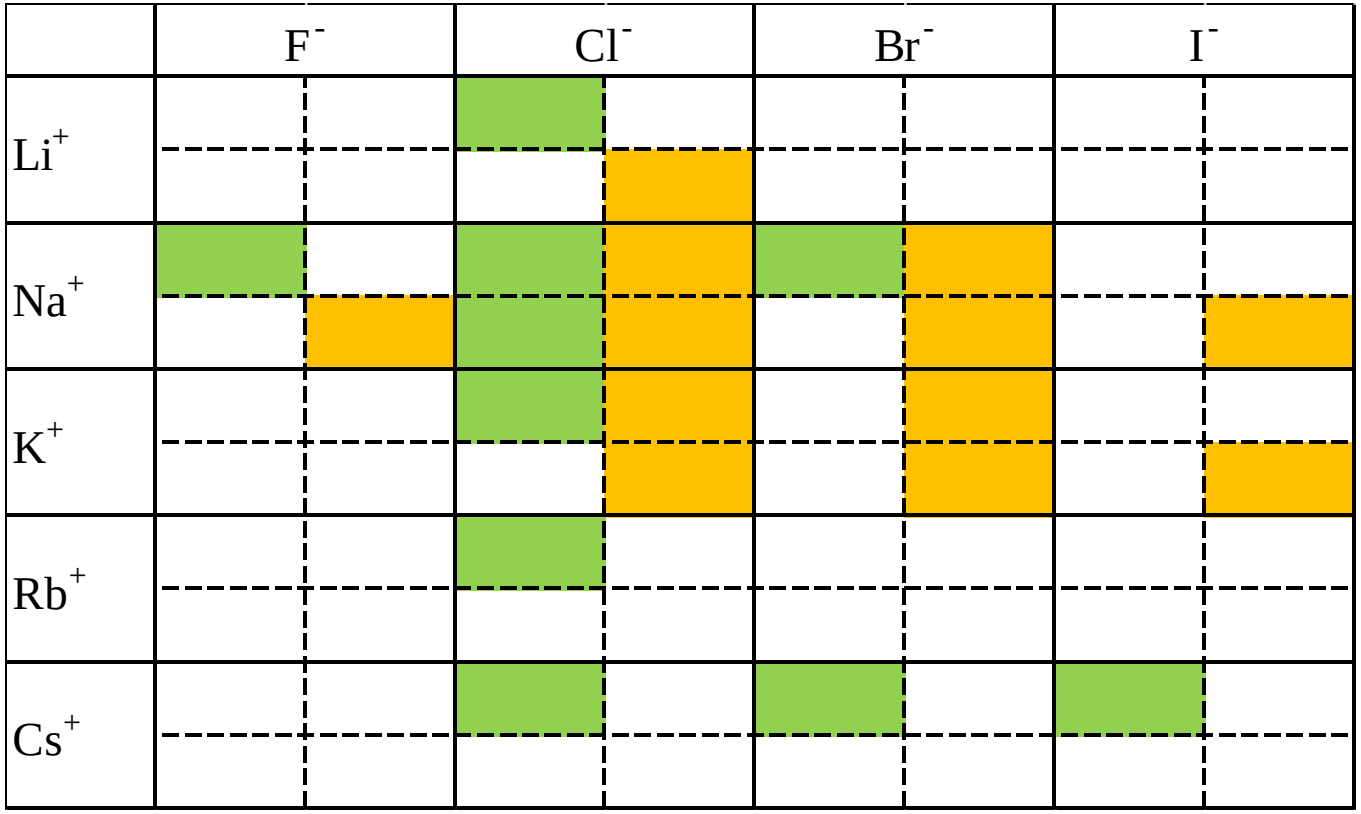
WATER + SALT

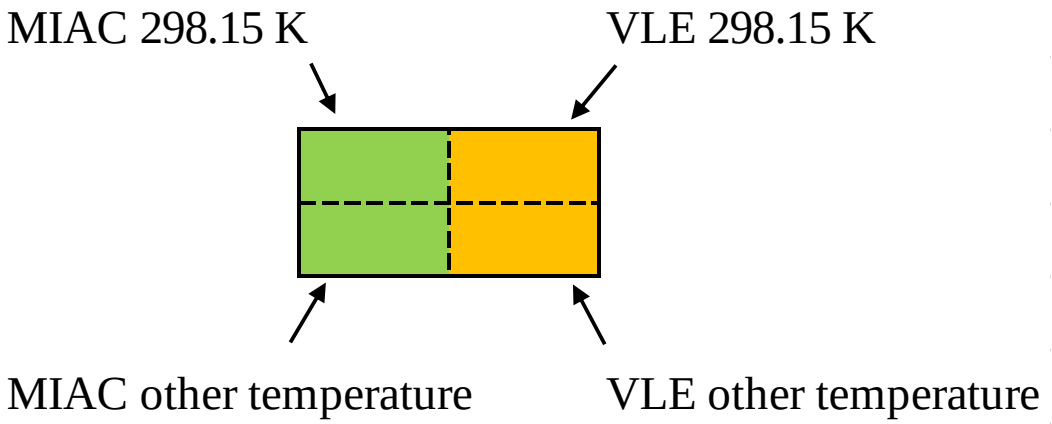
MIAC vs molality

	Li	Na	K	Rb	Cs
F	NO DATA				
Cl					
Br					
I					

Santiago Vaque Aura et al: « Data analysis for electrolyte systems : a method illustrated on alkali halides in water » 2021, JCED, Vol 66, p 2976-2990

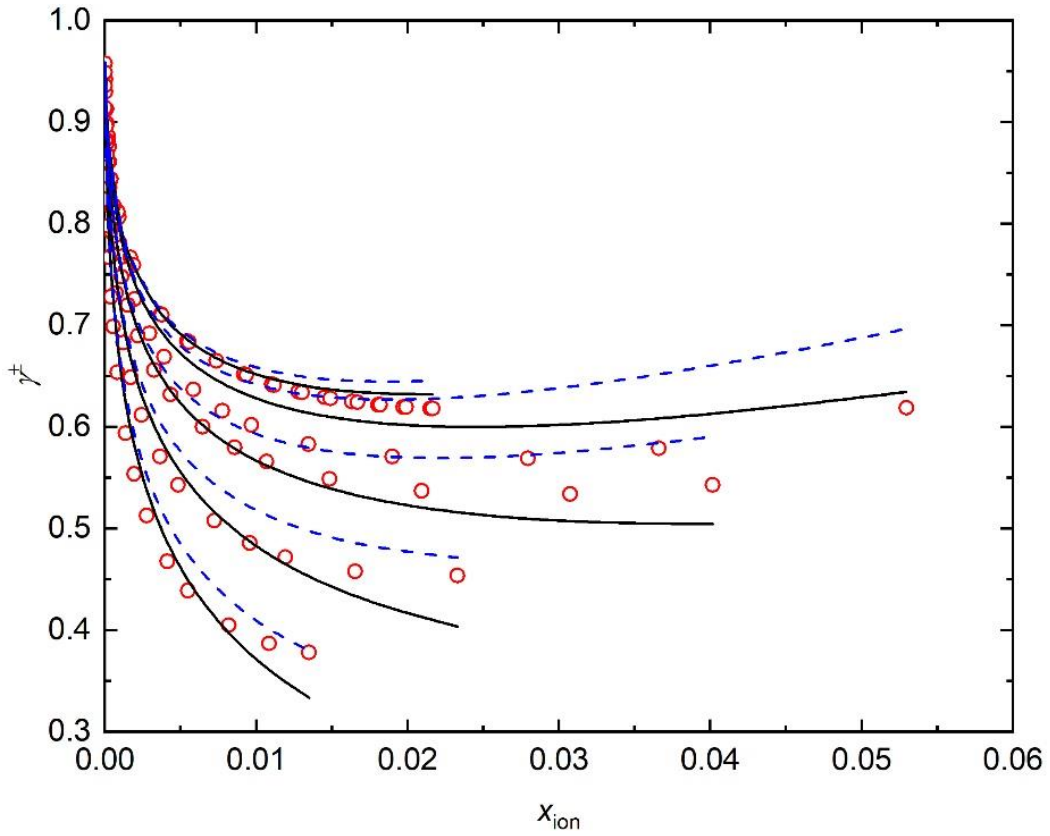
WATER + METHANOL + SALT



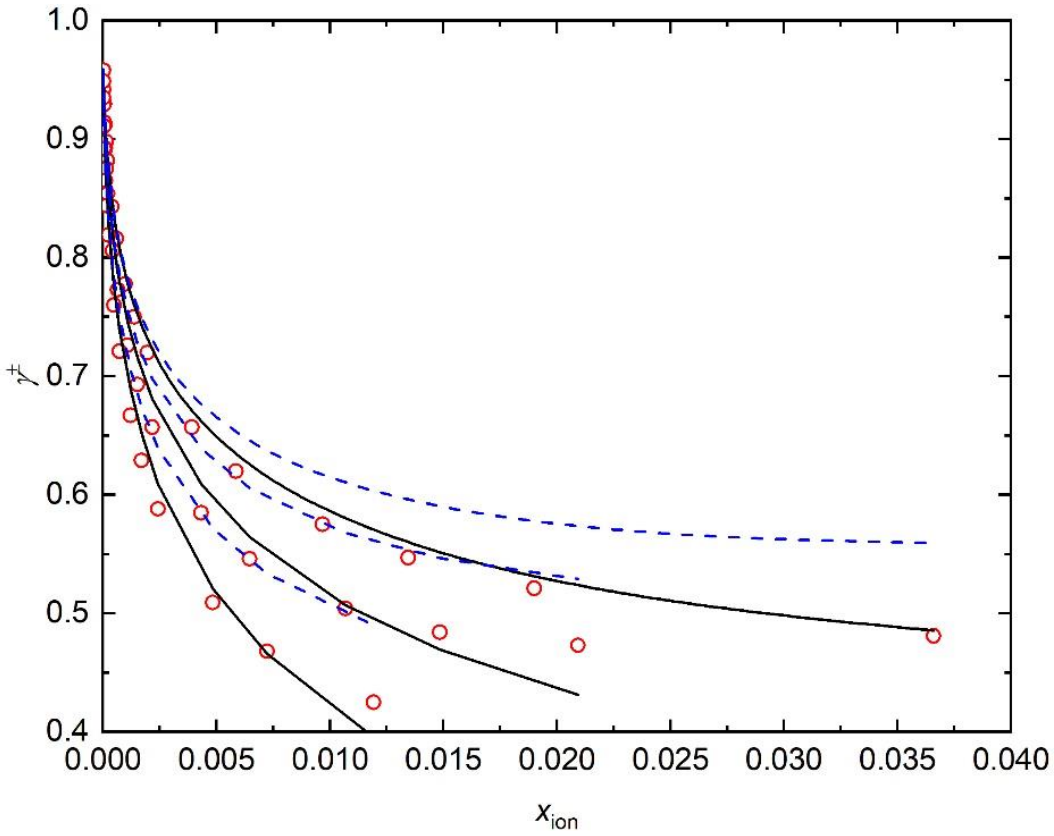


WATER + SALT + ALCOHOL

Water + methanol + NaCl



Water + methanol + KCl

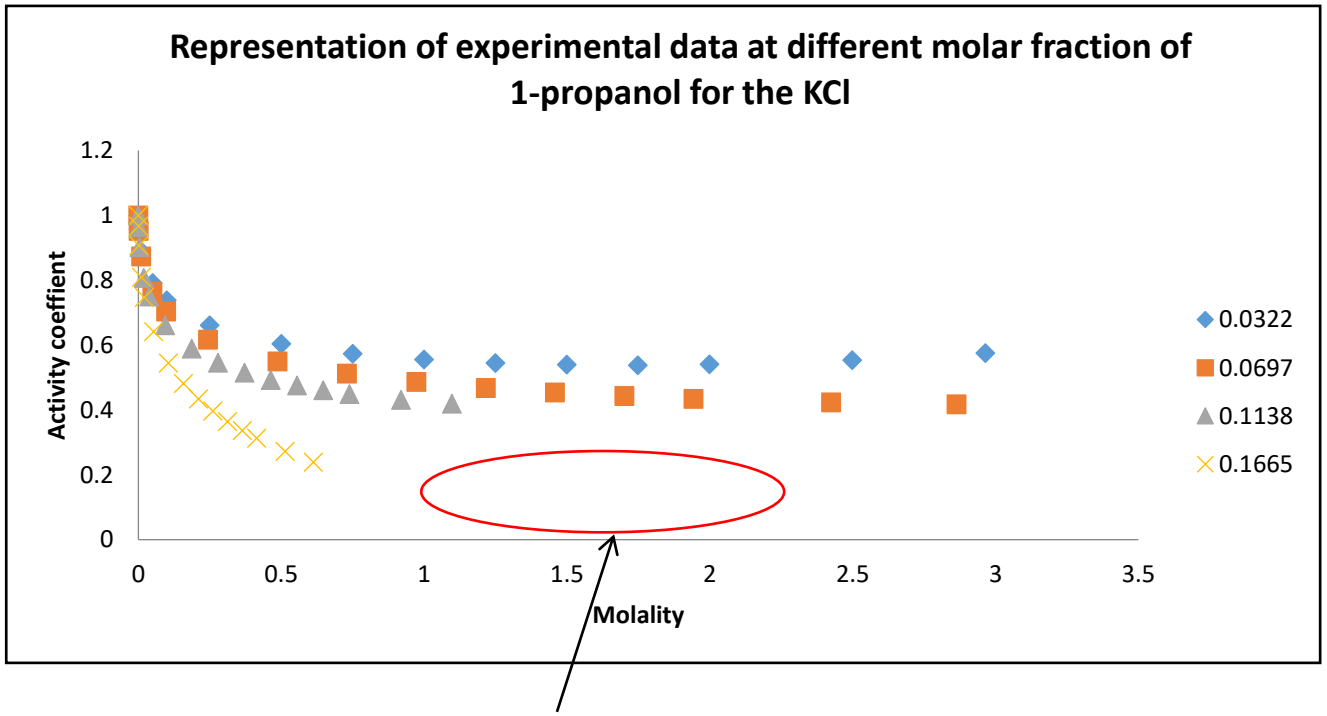


Black solid lines: optimized parameters

Blue dashed lines: $\tau_{salt\text{-}alcohol} = -4$, $\tau_{alcohol\text{-}salt} = 8.5$

Yang et al. : »A Benchmark Database for Mixed-Solvent Electrolyte Solutions: Consistency Analysis Using E-NRT » 2022, IECR, Vol 61, 42, 15576-15593

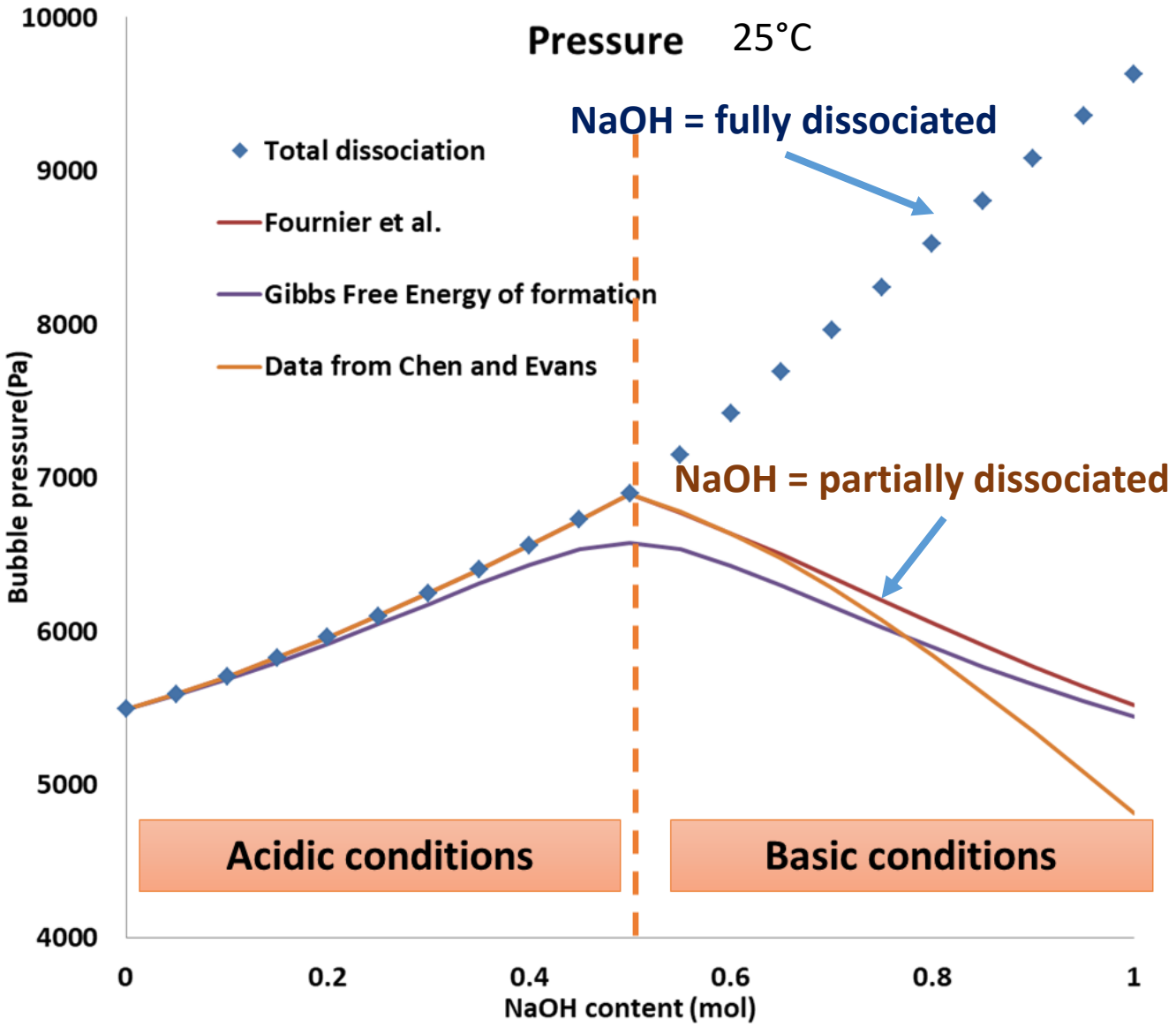
ACTIVITY COEFFICIENT OF WATER + 1-PROPANOL

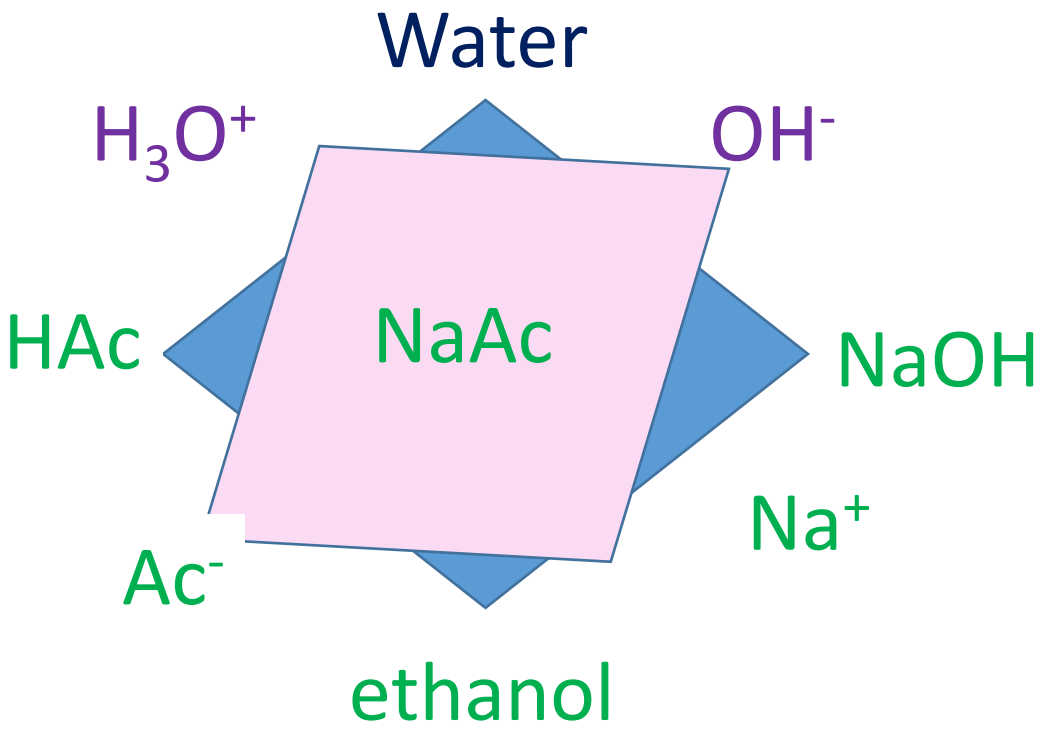


We need more data of activity coefficient at higher molar fraction of 1-propanol

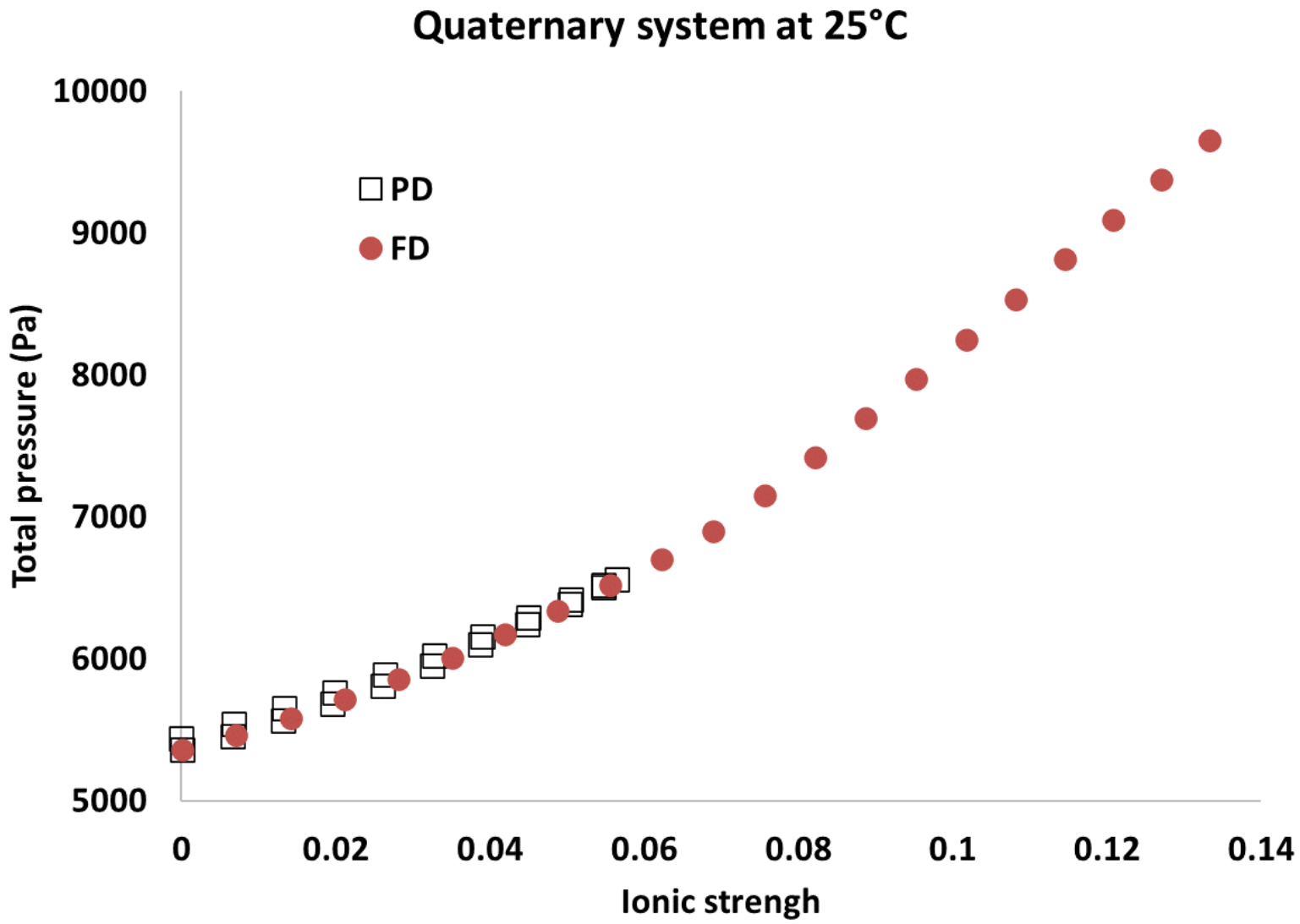
QUATERNARY

Consider 10 moles of water; 3 moles of ethanol and 1 mol of « salt » (NaOH + Hac)





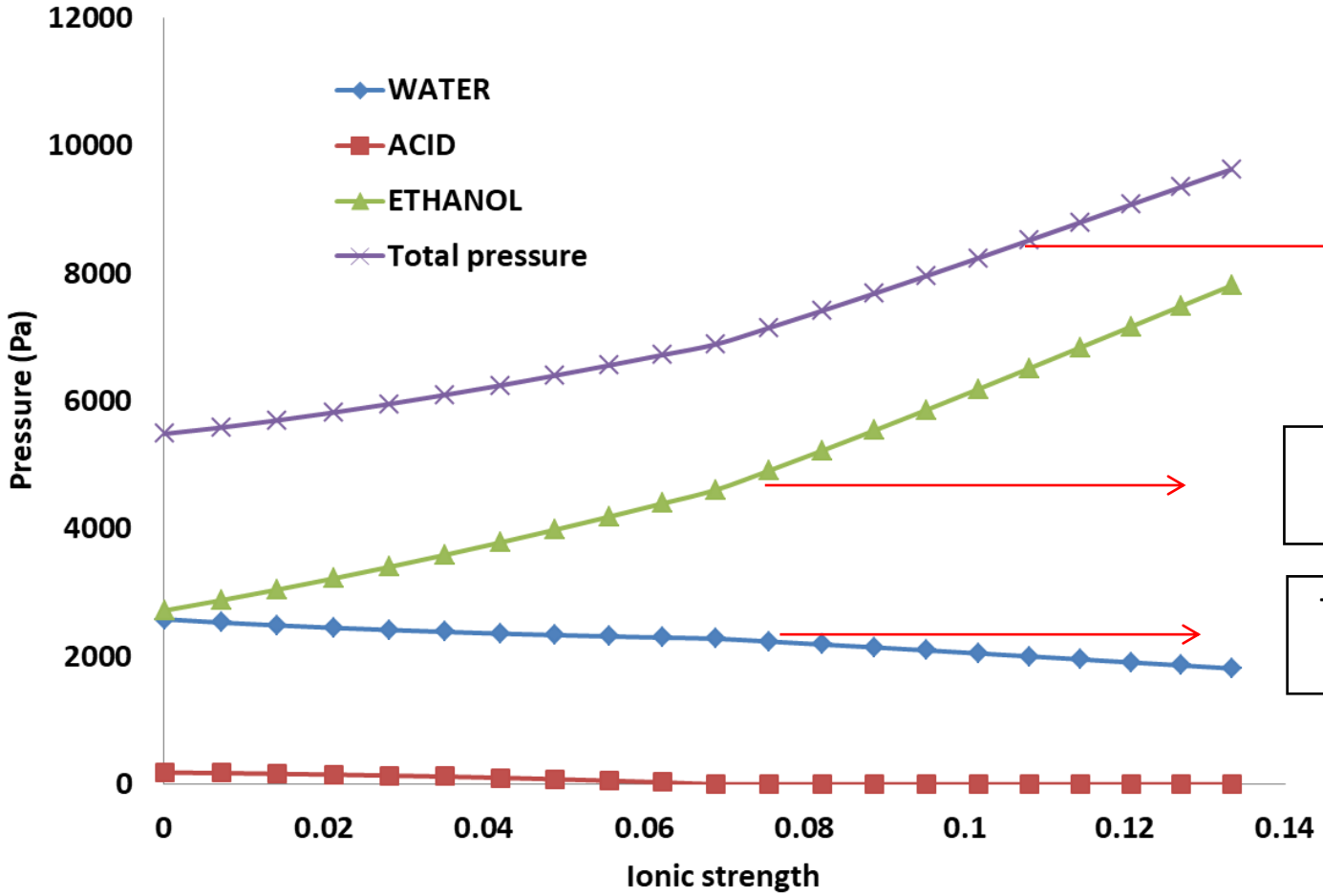
PRESSURE IS ALMOST DIRECTLY RELATED TO IONIC STRENGTH!



CALCULATIONS AT DEFAULT CONDITIONS (VALUES)

$$P_i = x_i \gamma_i P_i^{sat} \qquad P_{total} = \sum P_i$$

No ions in vapor phase.



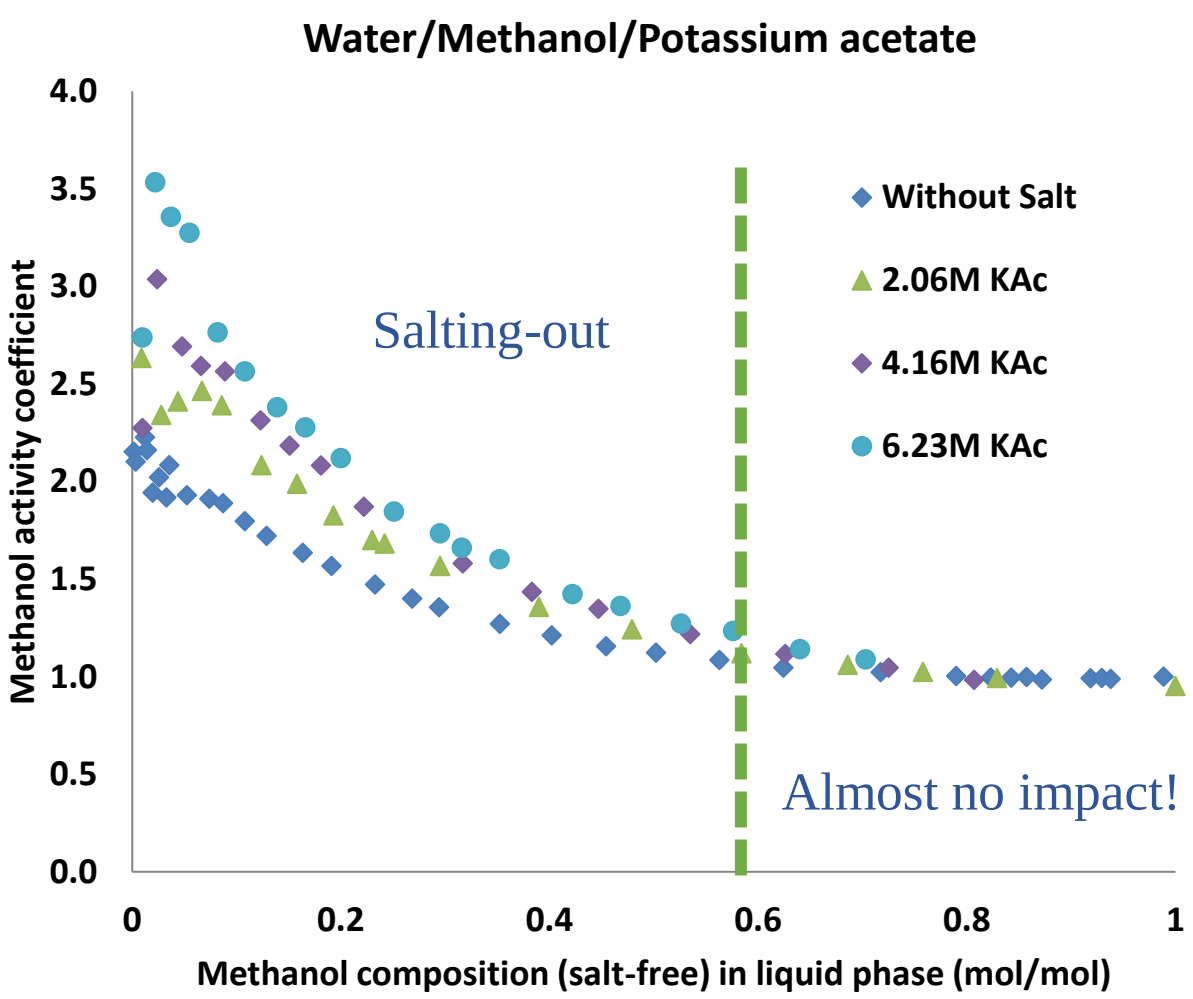
The salting-out effect of ethanol is greater than salting-in of water.

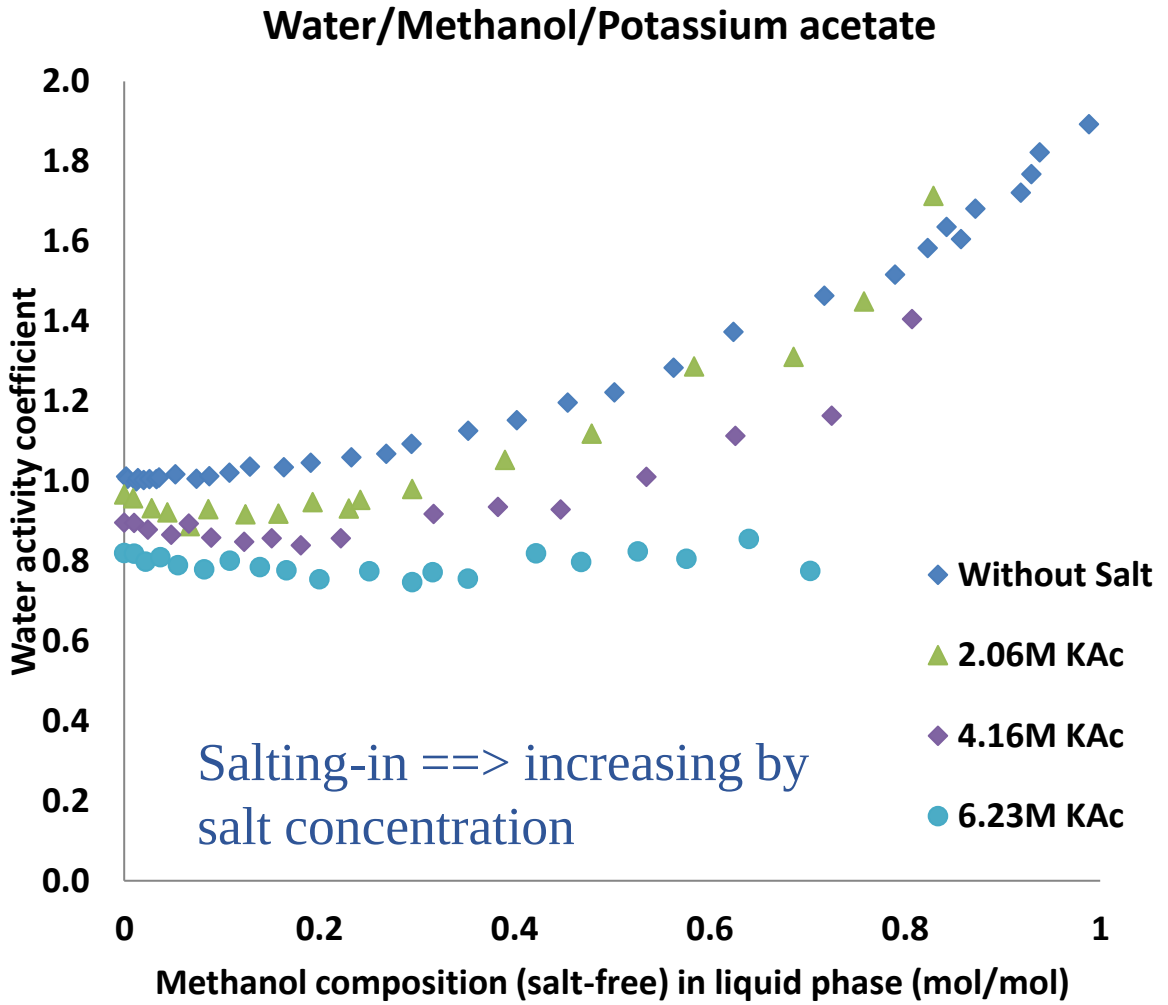
Vapor pressure of Ethanol increases as the ionic strength increases.

The greater the ionic strength, the lower the vapor pressure of the water.

DATA ANALYSIS

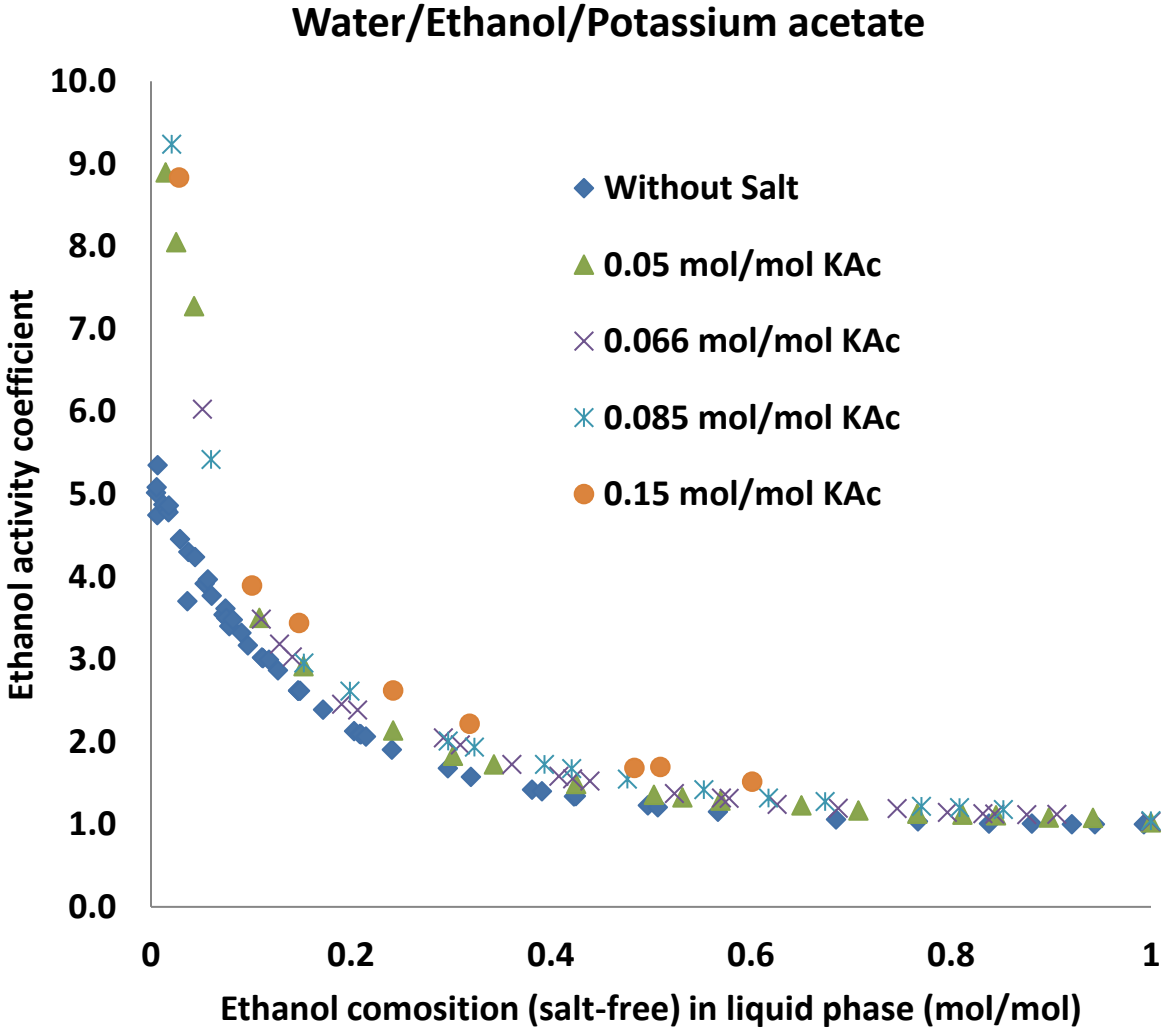
$$\gamma_i = \frac{y_i \times P}{x_i \times P_i^{\sigma}}$$

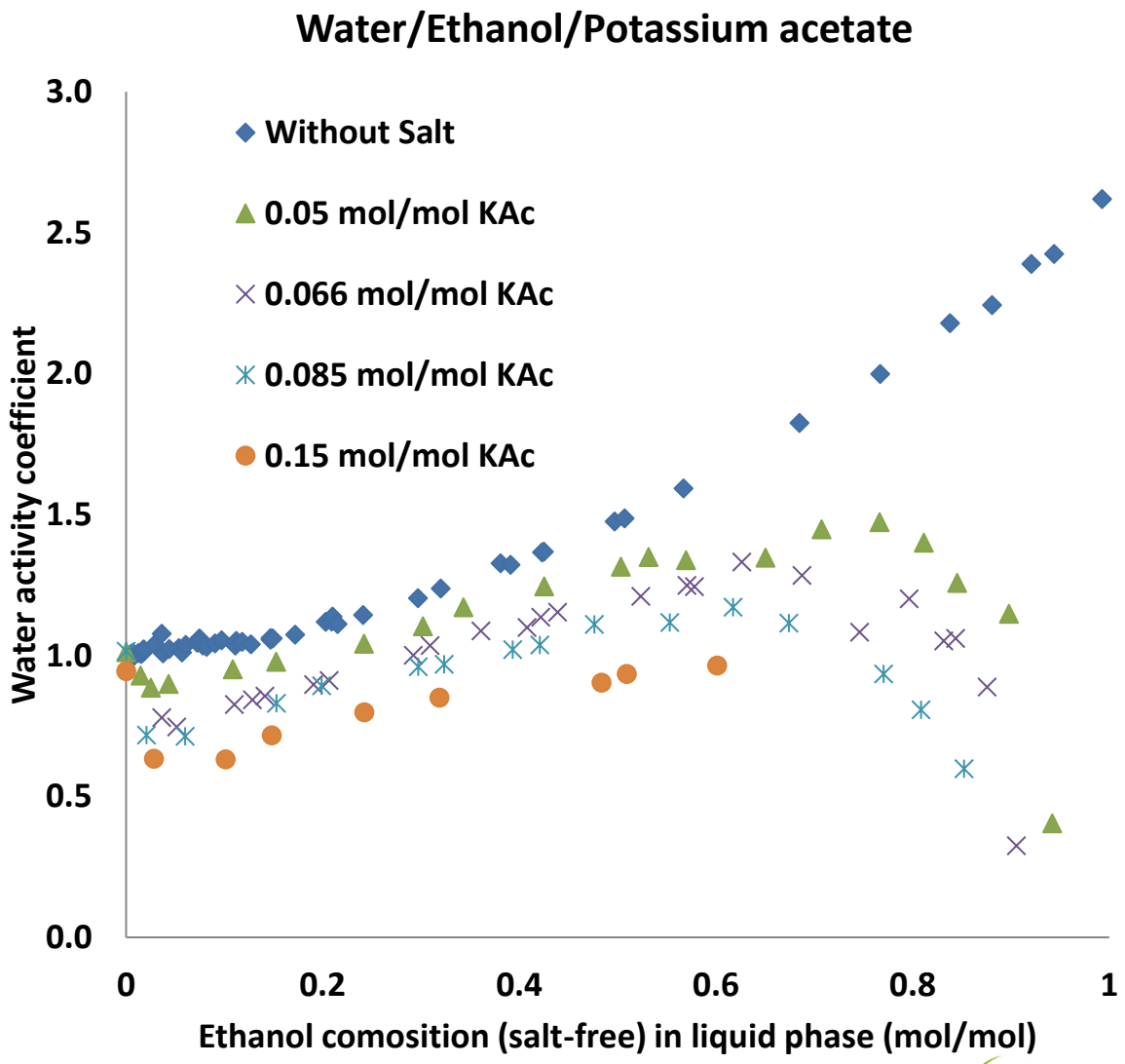




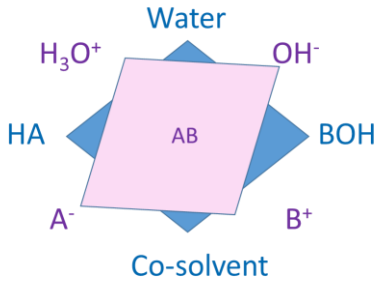
DATA ANALYSIS

$$\gamma_i = \frac{y_i \times P}{x_i \times P_i^{\sigma}}$$





LEVEL OF INVESTIGATION



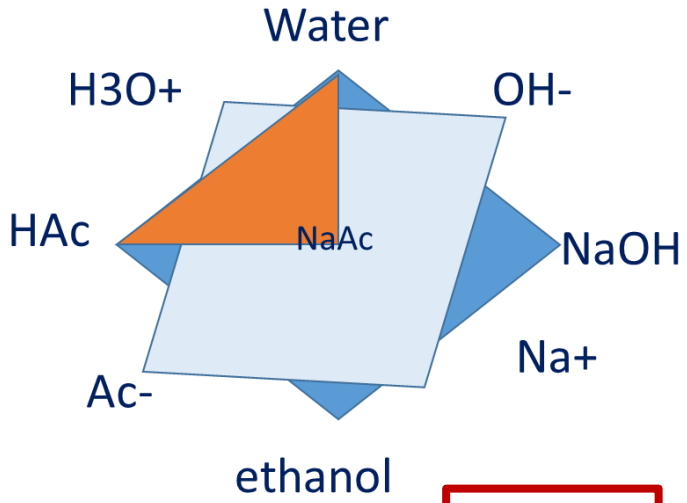
- Level 1: apparent composition
  - May be convenient when only apparent properties are needed (here solvent properties)
- Level 2: true composition
  - Many more species to parameterize

Apparent	True	Liquid	vapour	solid
water	water	x	x	
	H3O+	x		
	OH-	x		
cosolvent	cosolvent	x	x	
	HA	x	x	
A-	A-	x		
	BOH	x	x	
B+	B+	x		
	AB	x		x

We select here this solution because that is what industrial partners use (eNRTL within Aspen)
+
Ionic strength is made visible

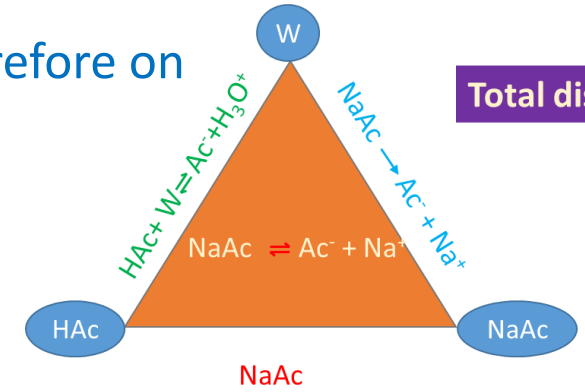
INVESTIGATION USING DATA

- Ternary
  VLE (isobar : 1 bar, T = 375-393K)
  Vercher,E.;Vazquez,M.I.;Martinez-Andreu,A., J. Chem. Eng. Data 48 (2003) 217-220.



- **Objective** = relative volatility of molecular species in presence of salts

- Ion pairing should be considered always
  - Has a large effect on ionic strength and therefore on volatilities



Total dissociation!

No dissociation!

W+NaAc

- MIAC (298.15K)
  R.A. Robinson, R.H. Stokes, T.Faraday Soc. 45 (1949) 612–624.
  O.D. Bonner, J.Sol.Chem. 17 (1988) 999–1002
- VLE (isotherms : 278.15-310K)
  R.A. Robinson, R.H. Stokes, T.Faraday Soc. 45 (1949) 612–624.
- VLE (isobar : 1 bar = 372-382K)
  E. Vercher, M.I. Vázquez, A. Martínez-Andreu, J. Chem. Eng. Data 48 (2003) 217–220.

- Binary HAc + NaAc
  VLE (isobar : 1 bar, T = 390-398K)
  Vercher,E.;Vazquez,M.I.;Martinez-Andreu,A., J. Chem. Eng. Data 48 (2003) 217-220.

MODELING + PARAMETERIZATION APPROACH

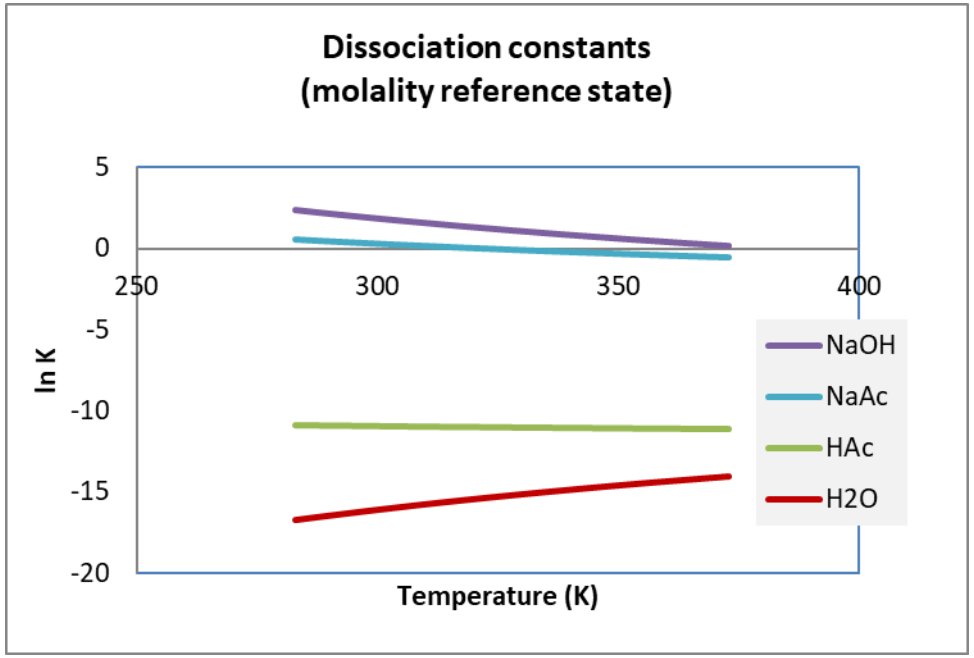
Modeling approach:

- CPA model in vapour phase with BIPs
- Activity coefficient in liquid phase calculated using eNRTL
  - Aspen parameters are kept if available and ***if possible***
  - Otherwise, NRTL parameter fitting,

Considered compounds:

Water	W	w
Sodium Acetate	NaAc	s
	Na+	i
	Ac-	i
Acetic acid	Hac	a

$$NaOH \leftrightarrow Na^+ + OH^-$$
$$NaAc \leftrightarrow Na^+ + Ac^-$$
$$HAc \leftrightarrow H^+ + Ac^-$$
$$H_2O \leftrightarrow H^+ + OH^-$$



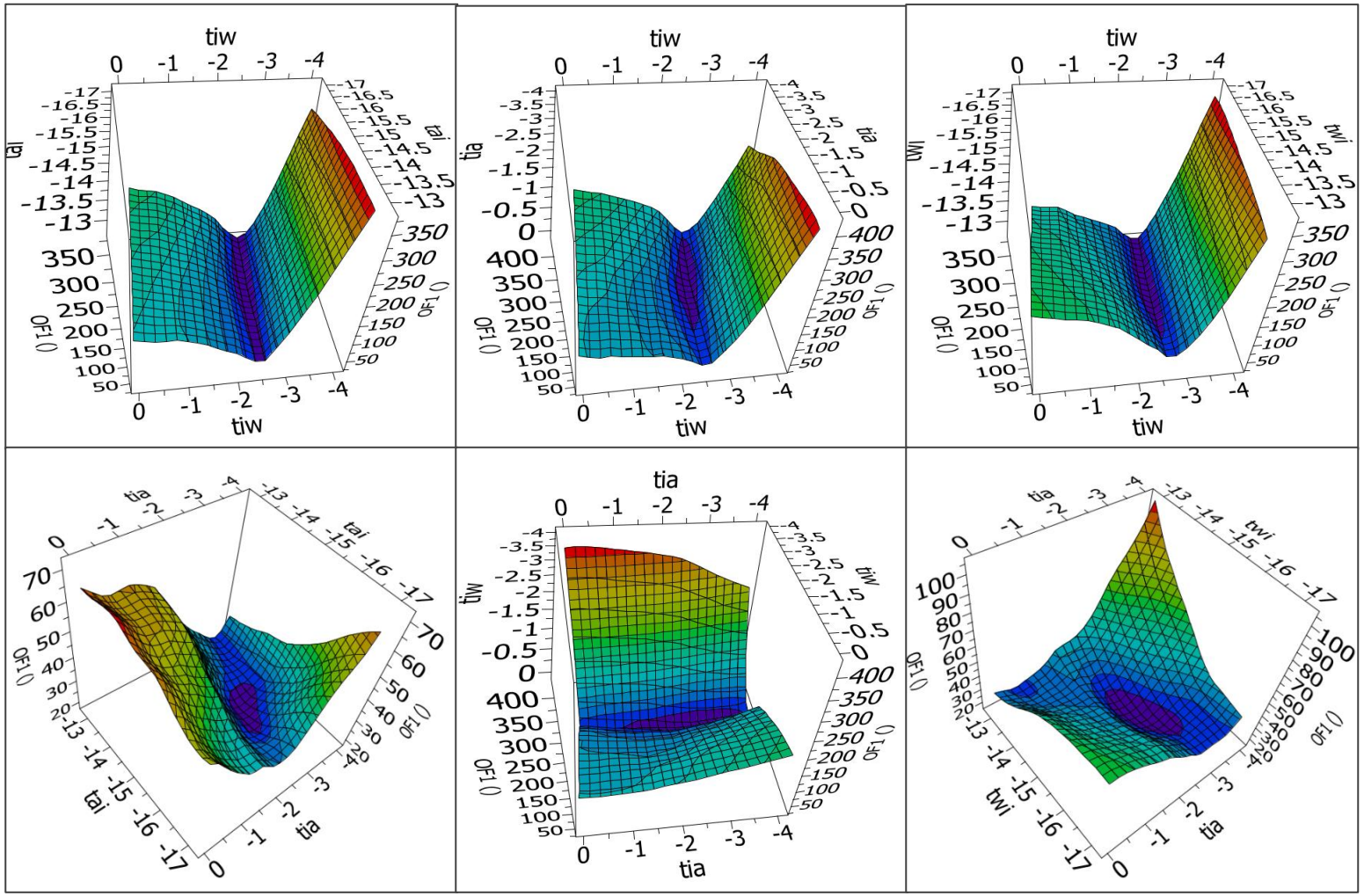
Proposed fitting approach

- τ_{ws}/ τ_{sw} from Aspen kept unchanged
- τ_{as}/ τ_{sa} fit on Hac-NaAc bin data
- τ_{ai}/ τ_{ia} & τ_{wi}/ τ_{iw} fit on W-NaAc bin and ter data

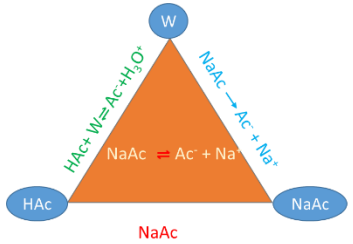
w : $water$
a : $acid$
i : $ions(Na^+, Ac^-)$
s : $salt(NaAc)$

WATER-IONS & HAC-IONS PARAMETER FITTING

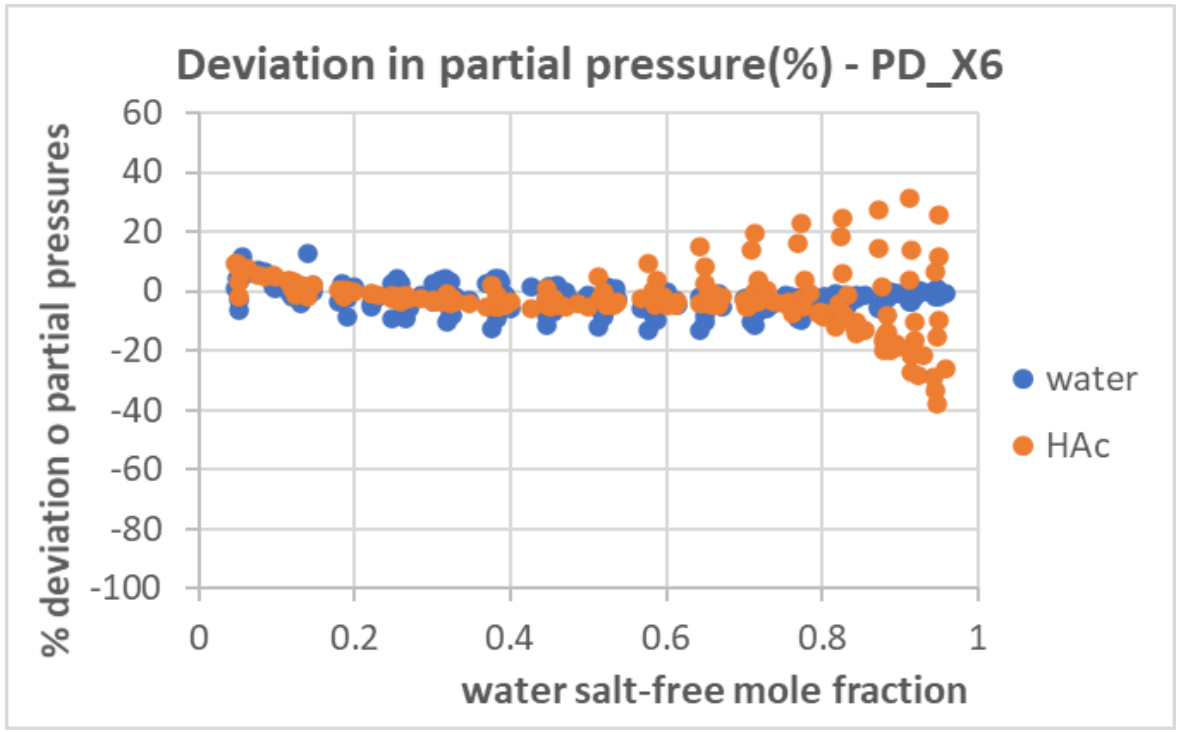
- In most of cases, response surfaces show valleys
  ➔ parameters are inter-correlated
- Valleys are very steep
  ➔ sensitive; wrong parameters may lead to irrealistic response
- **tiw** is most important, then **tia**
- Attempts have been made to reduce the number of parameters yet no significant success achieved



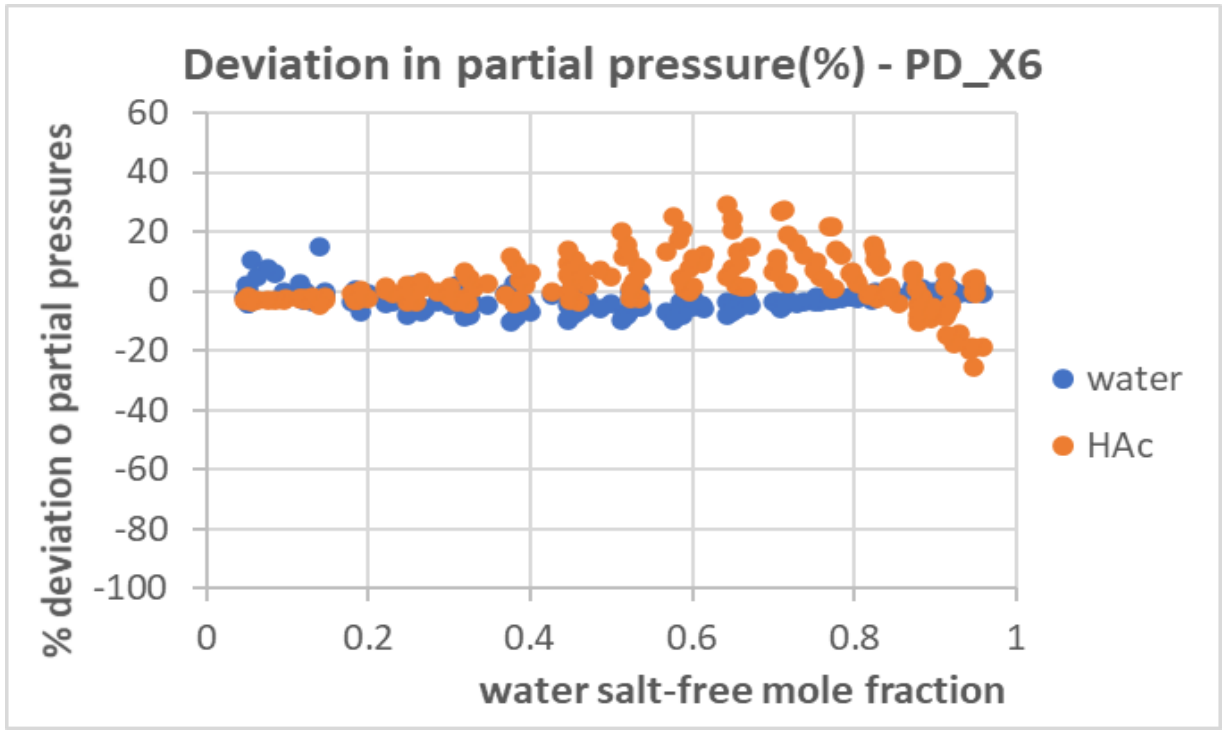
TERNARY PD



Parameter set AS1



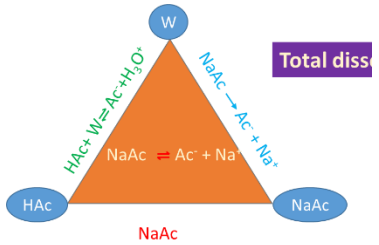
Parameter set AS2



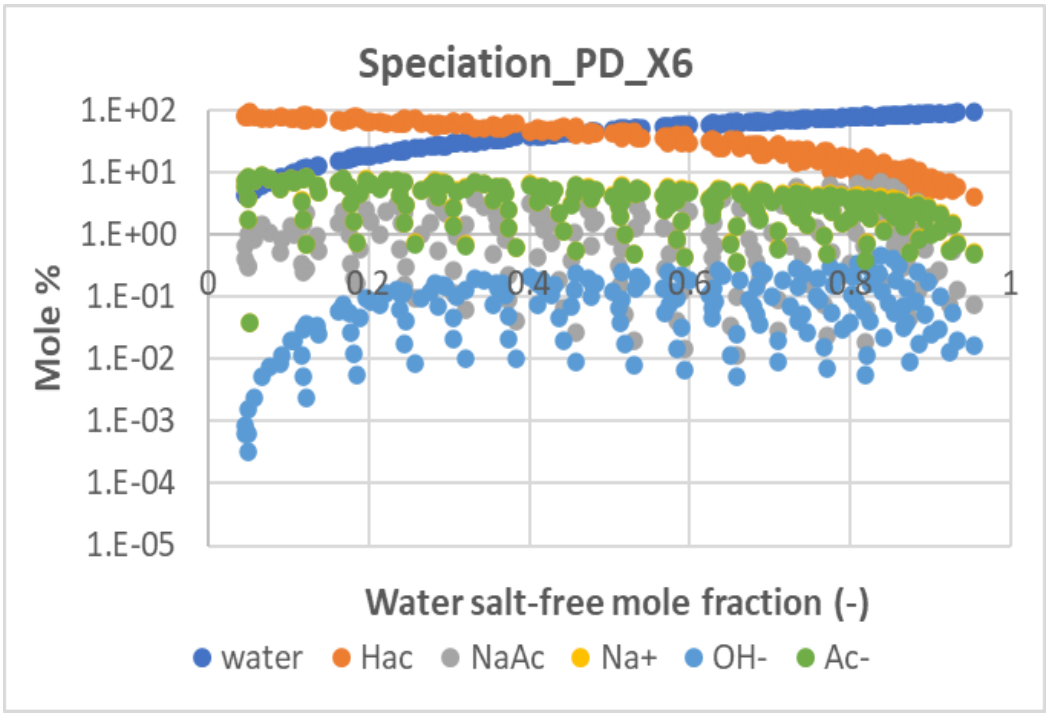
Reasonable deviations with regressed parameters

Two (at least) parameter sets provide equivalent results

4. TERNARY PD : SPECIATION

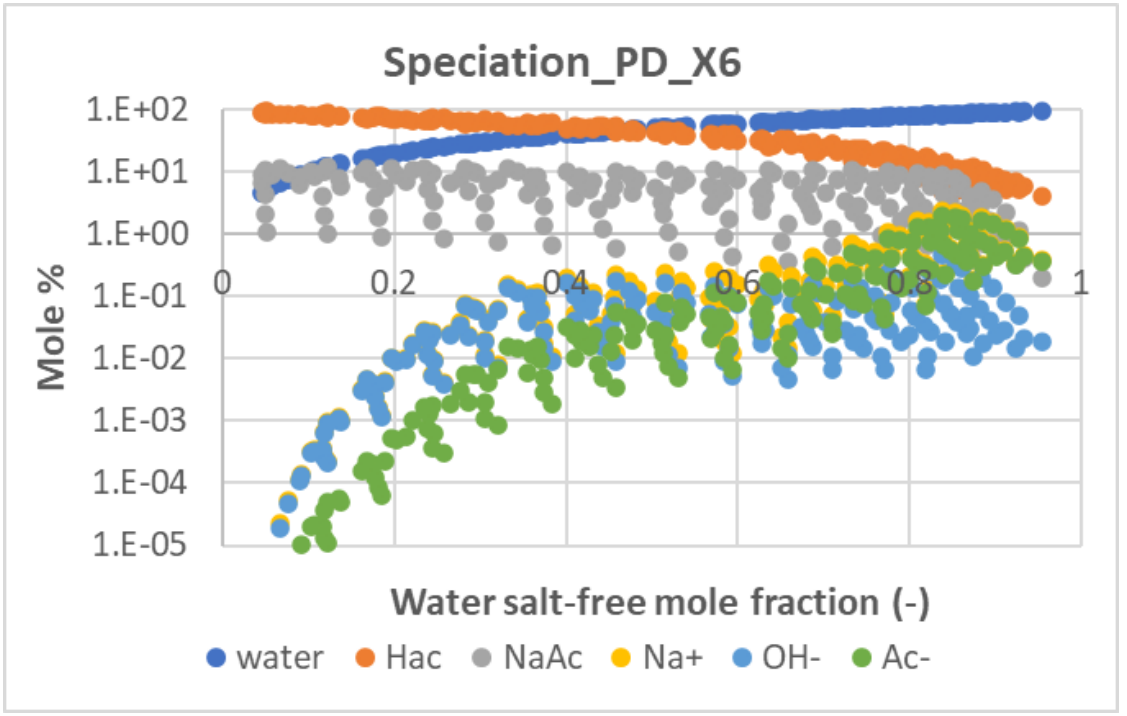


Parameter set AS1



- Na+ = Ac- > NaAc > OH-

Parameter set AS2



- NaAc > Na+ = OH- > Ac-

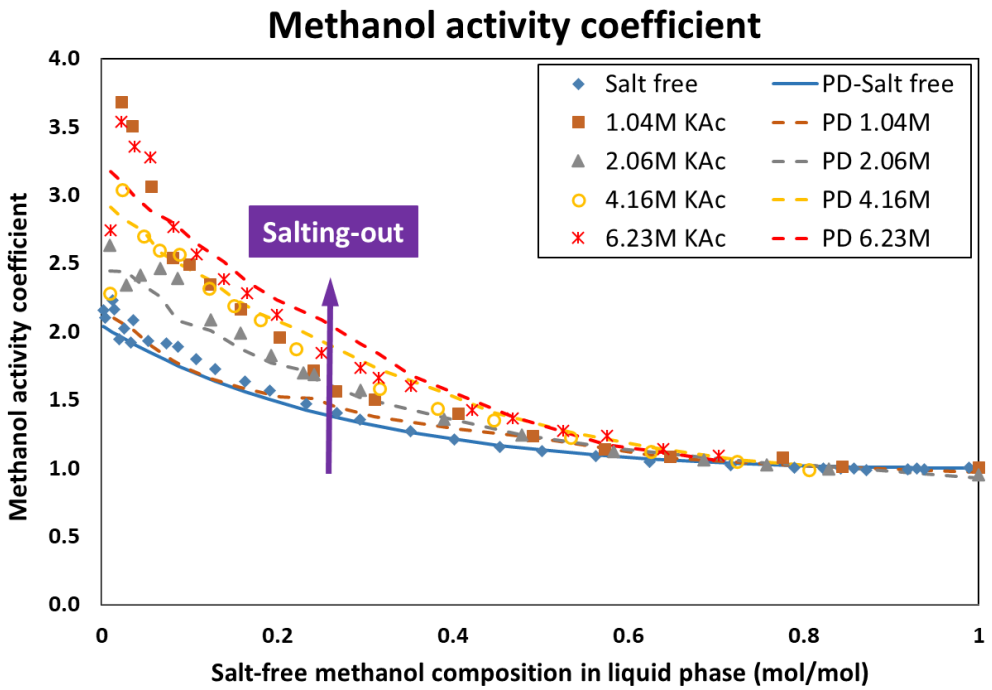
Speciation picture is very different!

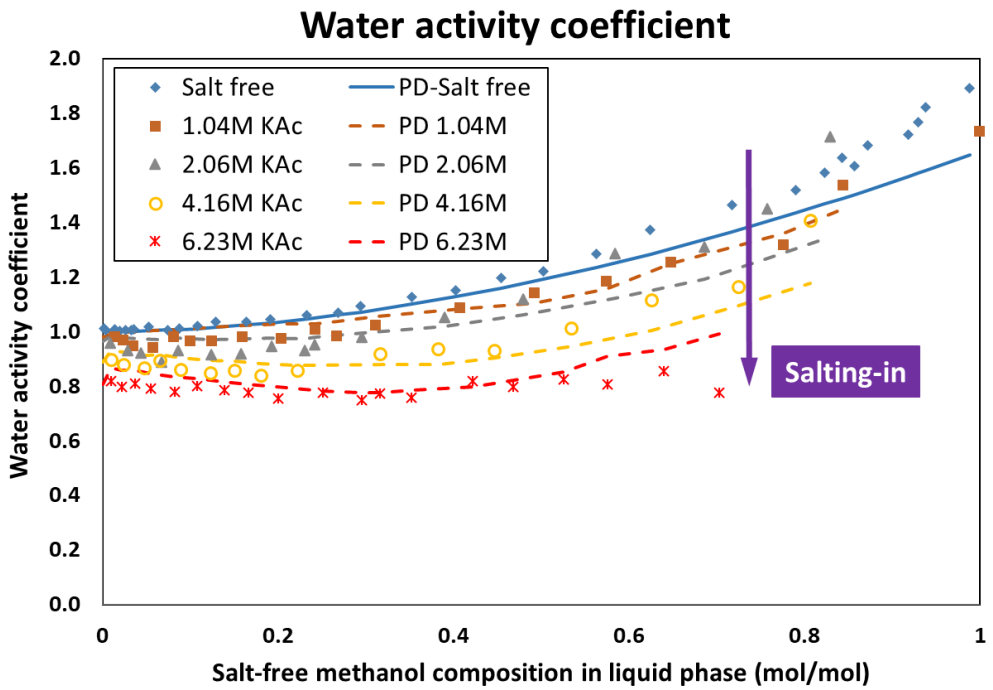
MODEL IMPACT ON SOLVENTS ACTIVITY COEFFICIENTS

Salting effect with MSI_2:

Activity coefficient of solvents can be estimated via VLE:

$$\gamma_i = \frac{y_i \times P}{x_i \times P_i^{\sigma}}$$

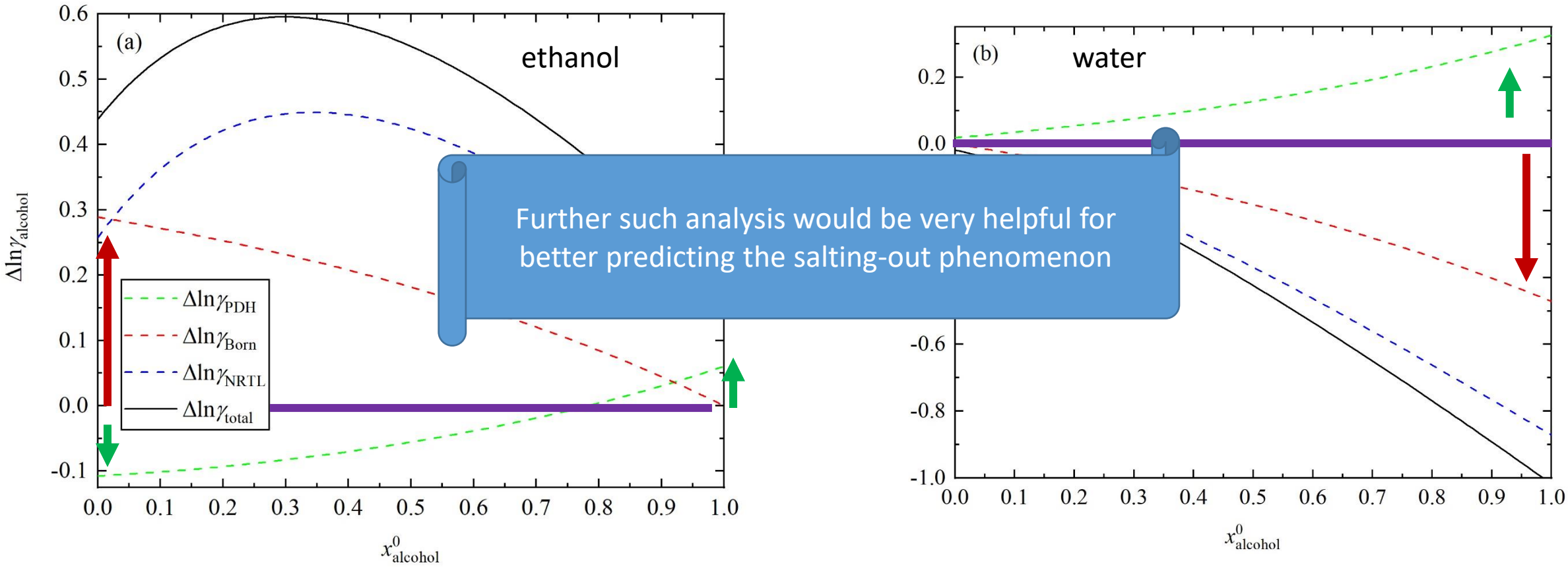




$$\frac{\gamma_i}{\gamma_i^{no\ salt}}$$ Measures salting in/out

SALTING OUT = EFFECT OF THE IONS ON THE ACTIVITY COEFFICIENT OF THE SOLVENTS

$$\Delta ln\gamma_i = ln\gamma_i^{x_{ion}=0.06} - ln\gamma_i^{no\ salt}$$



Contributions of the PDH, Born, and NRTL terms to the total $\Delta\ln(\gamma)$ for (a) alcohol, (b) water

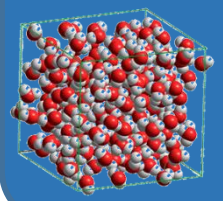
FINAL COMMENTS: SOME ACHIEVEMENTS WITHIN JIP

Data collection

➔**Internal consistency analysis:**
evaluate deviations from a consistent model (eNRTL)

➔**External consistency:**
evaluate trend in parameter values ;
Allows identifying missing data

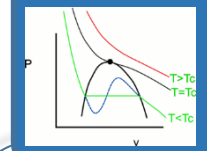
Advanced tools for validation & extrapolation



➔**Use statistical models**
- molecular simulation
- SAFT equation of state
- …

➔**Use graphical extrapolations**
Using adequate descriptors (model parameters)

Correlative models calibration



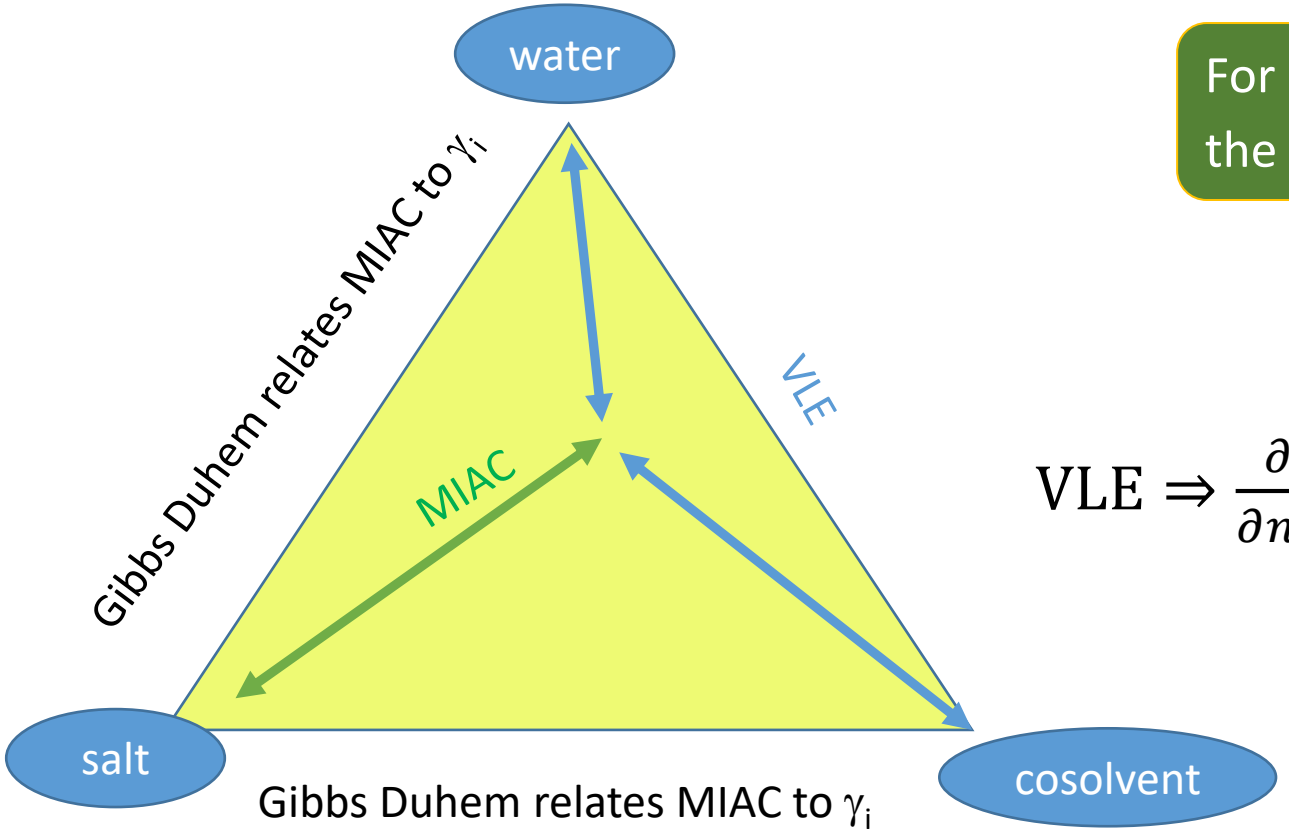
➔**Select validated data**
Various oigins so as to cover complementary information
➔**Construct objective function**
So that all subfunctions carry equivalent weight
➔**Analyze response surfaces**
Not all parameters are equally sensitive

For further progress on this topic:
- Quaternary data are missing
- Investigate link between salting in/out and speciation

WHICH PROPERTY?

Gibbs-Duhem links the two properties for binaries only

For evaluating salting out effect,
the solvent activity coefficient is more important



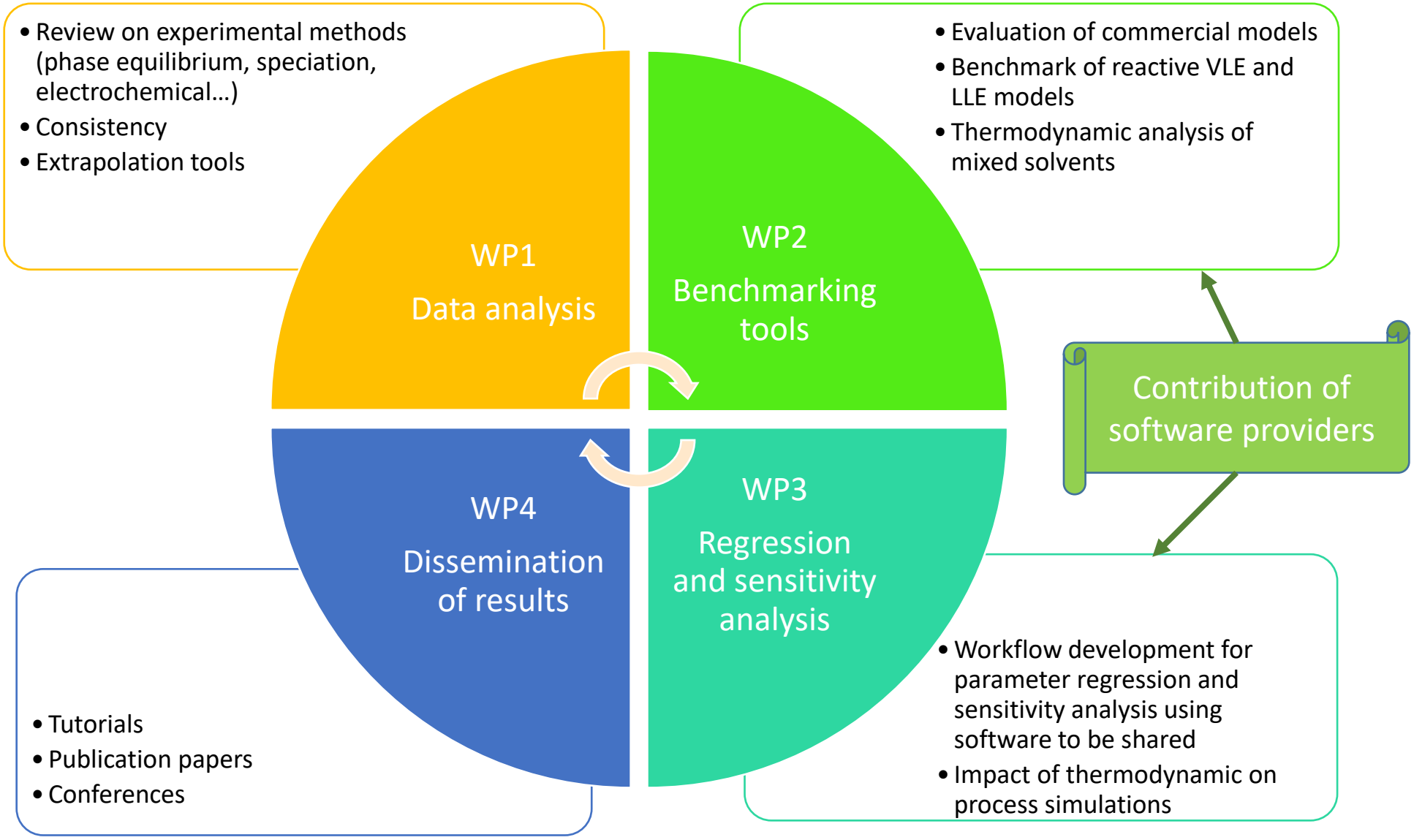
$$\text{VLE} \Rightarrow \frac{\partial G^{\text{E}}}{\partial n_{\text{solv}}} = \gamma_i$$

$$\text{SLE} \Rightarrow \text{MIAC} \Rightarrow \frac{\partial G^{\text{E}}}{\partial n_{\text{ion}}} - \frac{\partial G^{\text{E}}}{\partial n_{\text{ion}}}\Bigg|^{\text{Mixed Solve}}$$

$$\text{LLE} \Rightarrow \gamma_i \ \& \ \text{MIAC}$$

WORK WITHIN JIP2

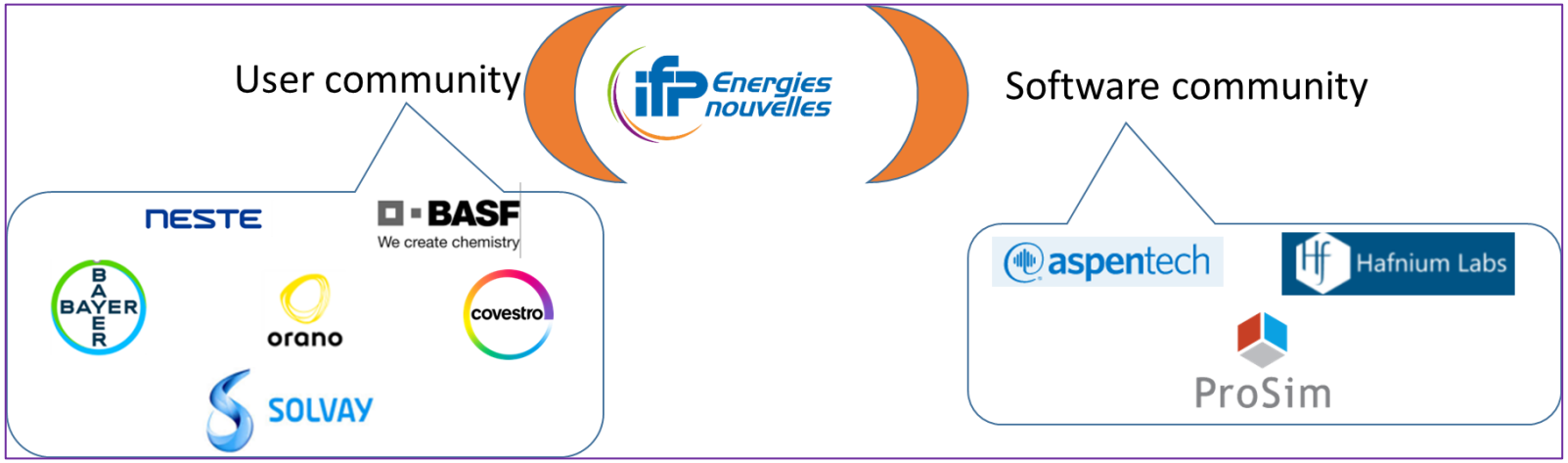
Work Packages



ACKNOWLEDGEMENTS

- JIP1 (2019-2022)

- JIP2 (2022-2025)



Still place for more !

- IFPEN
  - Santiago Vaque-Aura
  - Tri Dat Ngo
  - Saheb Maghsoodloo
  - Fufang Yang
  - Christos Tsanas

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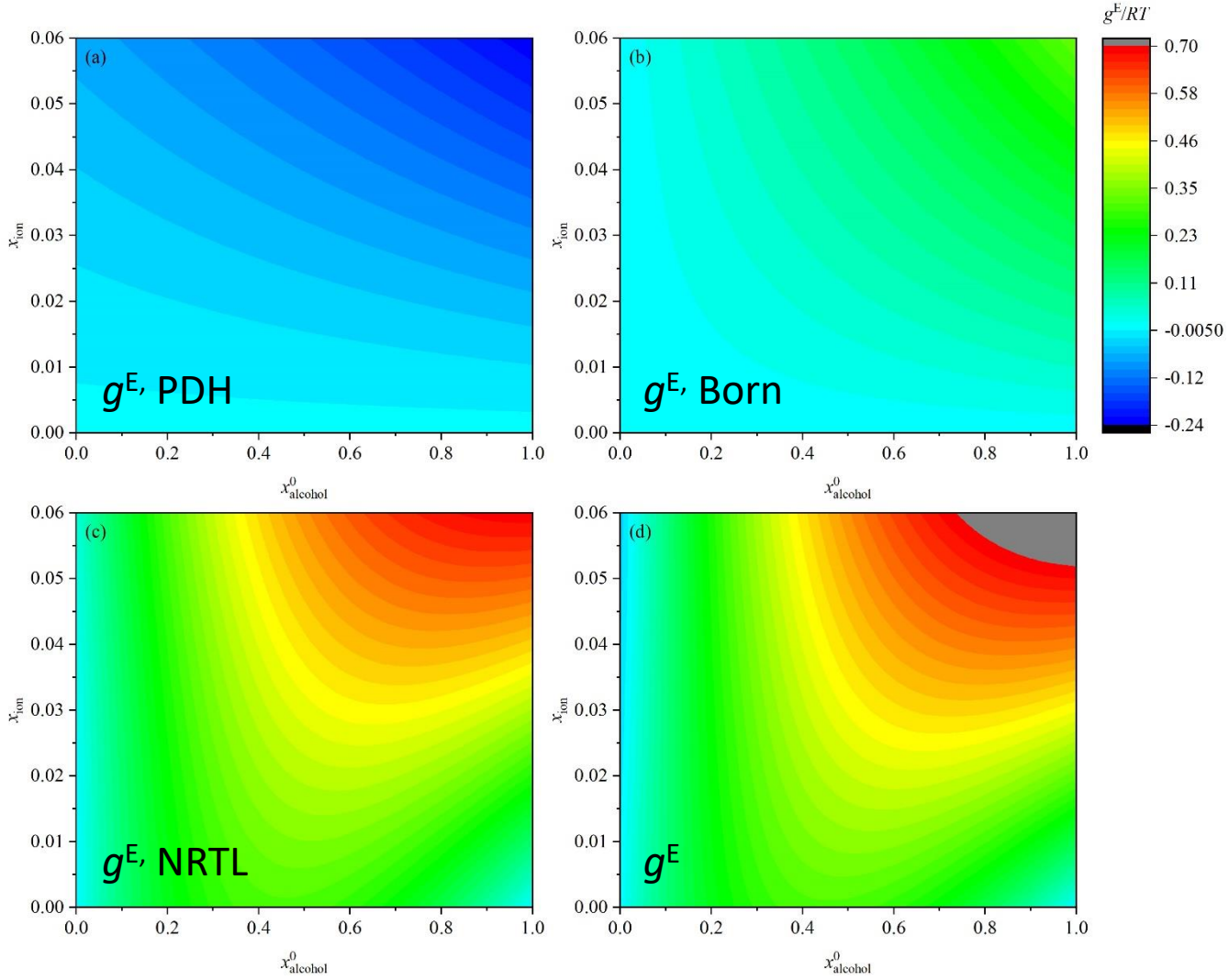
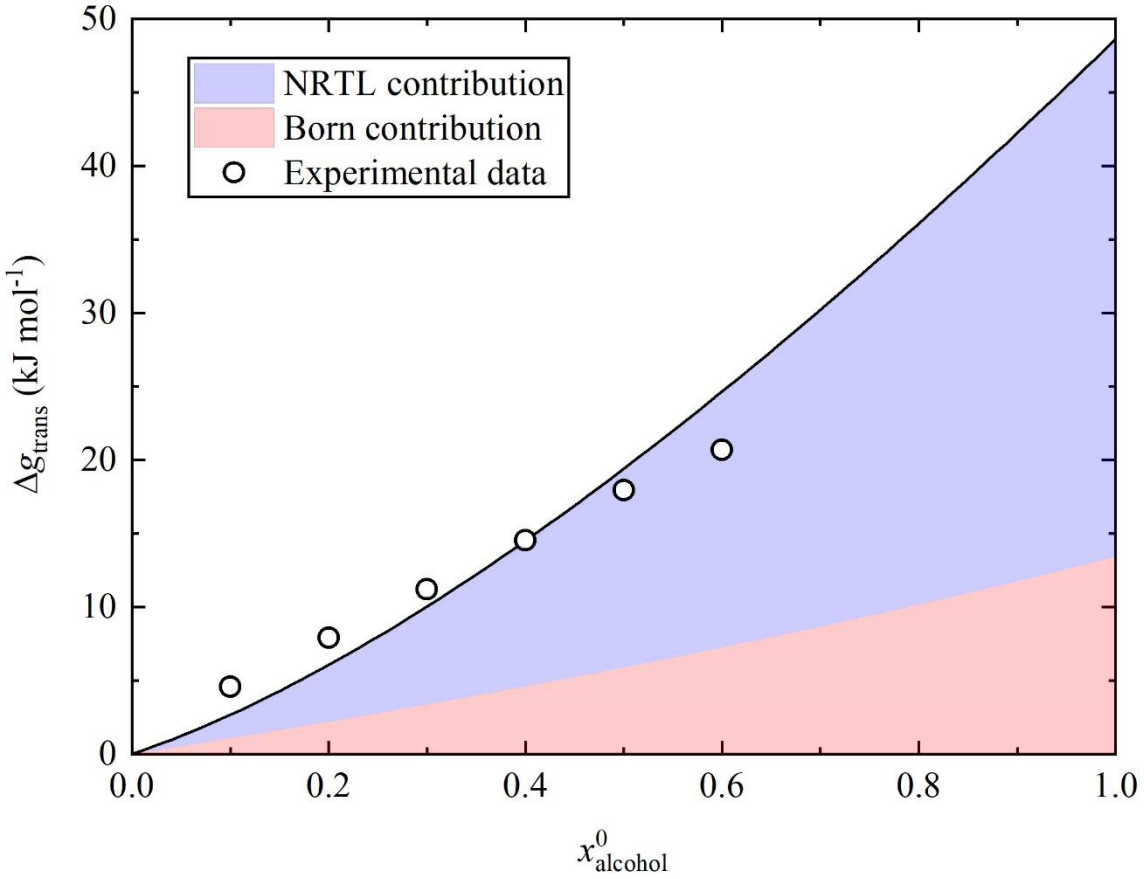
Contribution of the terms



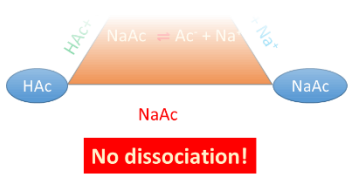
The behavior of the model is largely dominated by the NRTL term.

Gibbs energy of transfer



In contrast to what is usually claimed, the Born term on its own is not sufficient for describing the Gibbs energy of transfer.

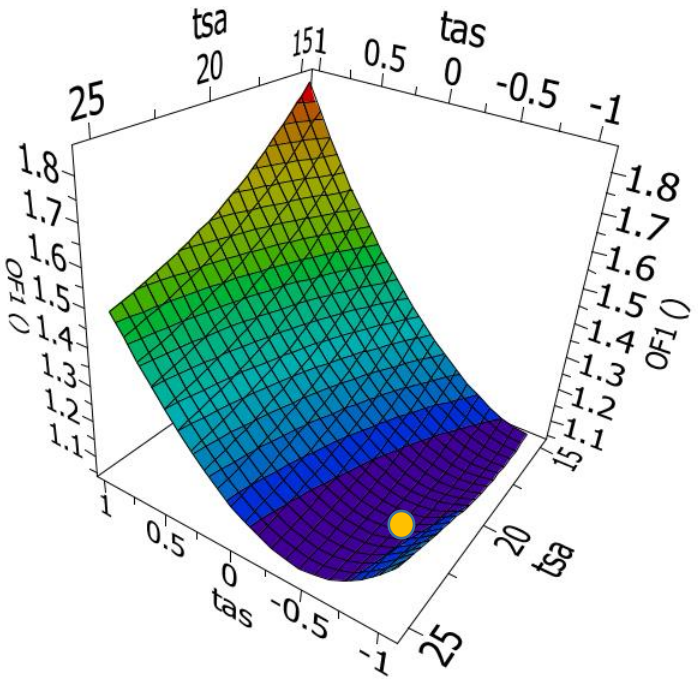
2. BINARY HAC-NAAC

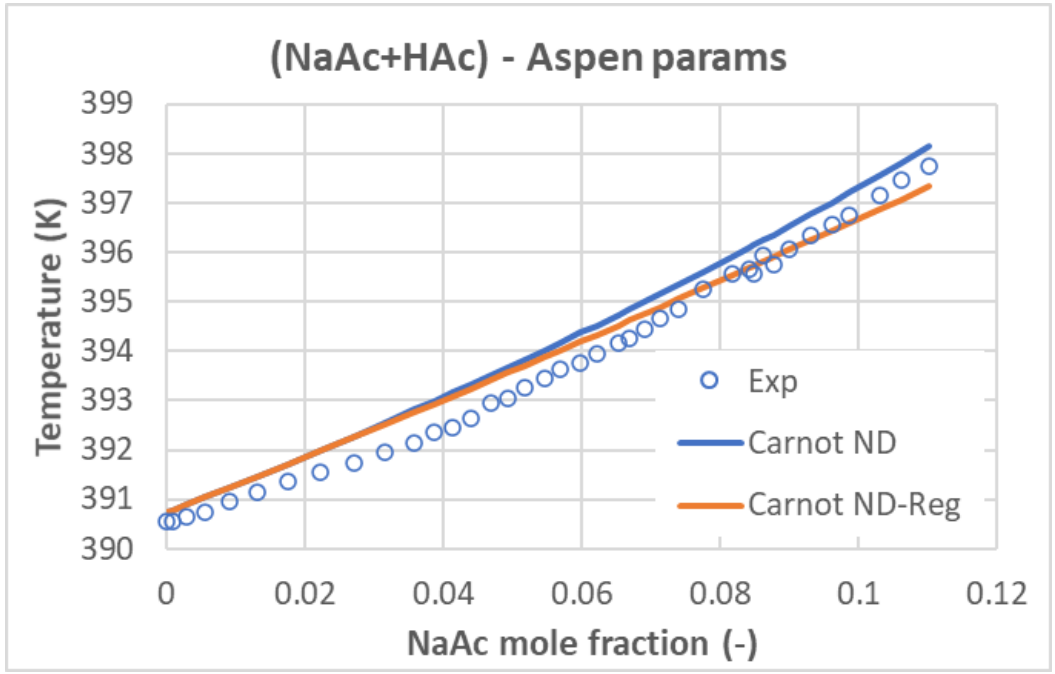


- Regression of **HAc-NaAc (a-s)** parameters

$$\tau_{ij} = \tau_{ij}^{0} + \tau_{ij}^{1}\left(\frac{1}{T} - \frac{1}{T_0}\right)$$

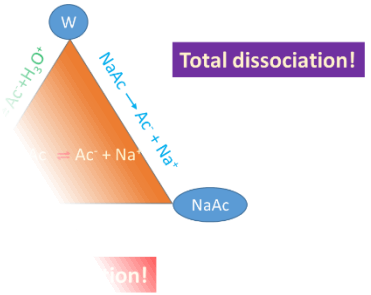
	Tij0	TijT	Tji0	TjiT	Alfaij	Origin
Hac-NaAc	-21.5843	0	2.74066	0	0.1	**Aspen**
Hac-NaAc	-0.75845	0	22.45050	0	0.1	**REG_VLE**





 |

3. BINARY WATER-NAAC



ÉNERGIES NOUVELLES

- MIAC (298.15K)

R.A. Robinson, R.H. Stokes,
T.Faraday Soc. 45 (1949) 612–624.

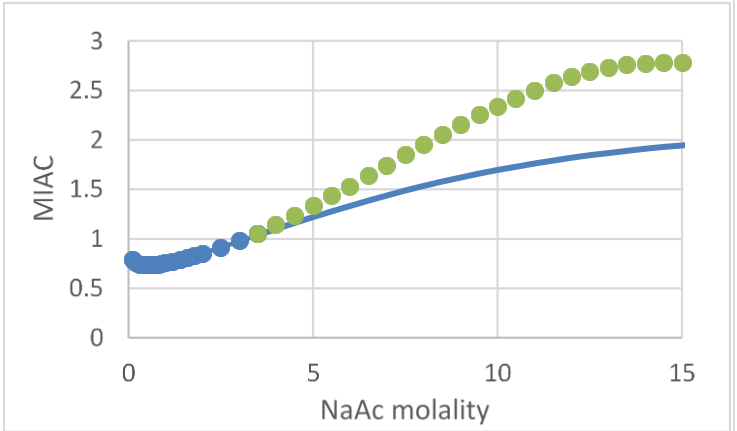
O.D. Bonner, J.Sol.Chem. 17 (1988) 999–1002

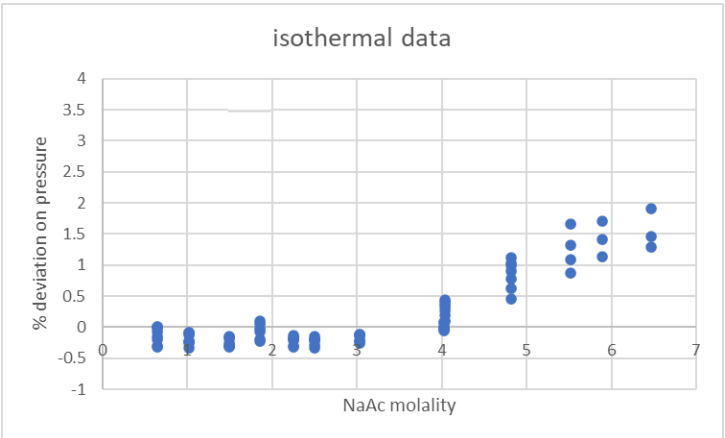
- VLE (isotherms : 278.15-310K)

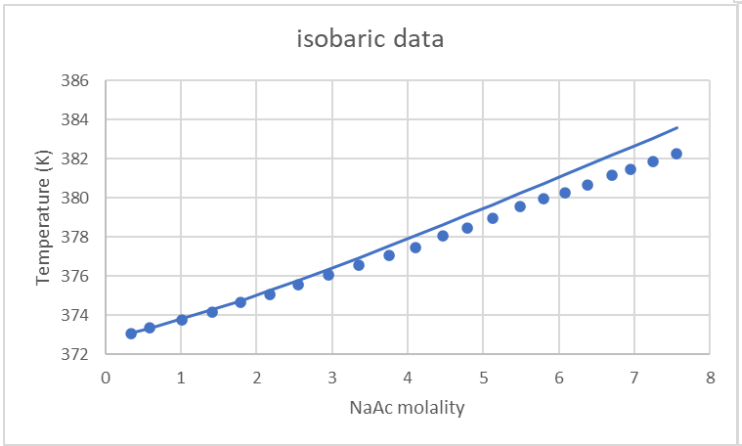
R.A. Robinson, R.H. Stokes,
T.Faraday Soc. 45 (1949) 612–624.

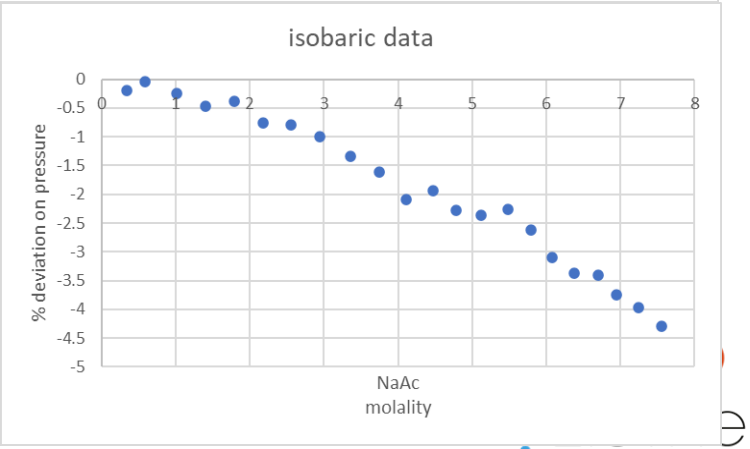
- VLE (isobar : 1 bar = 372-382K)

E. Vercher, M.I. Vázquez, A. Martínez-Andreu,
J. Chem. Eng. Data 48 (2003) 217–220.









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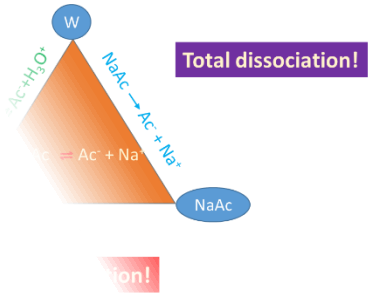
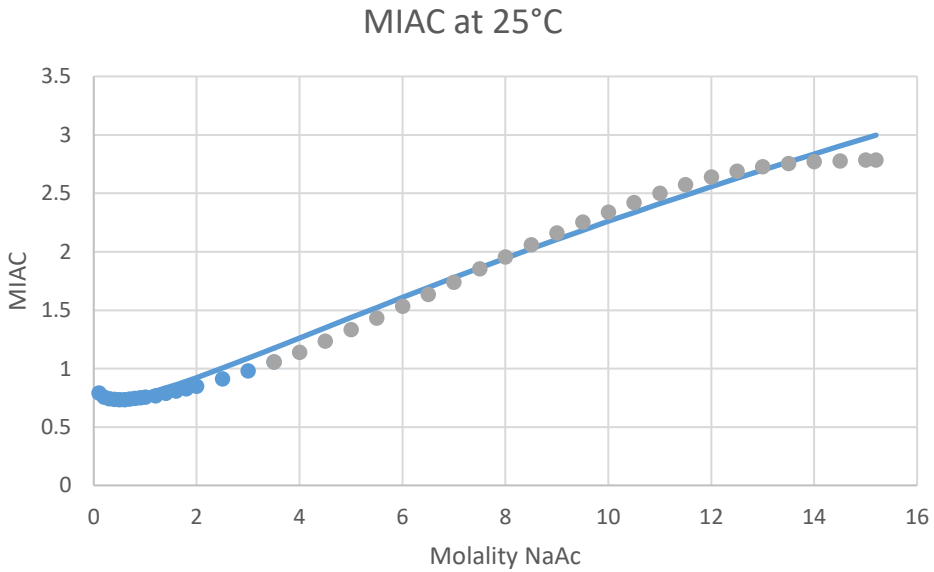
Aspen parameters, FD option

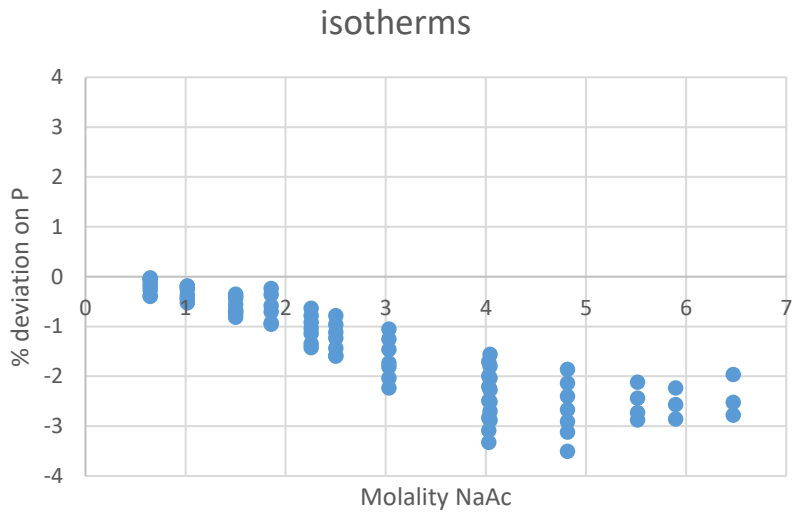
3. BINARY WATER-NAAC

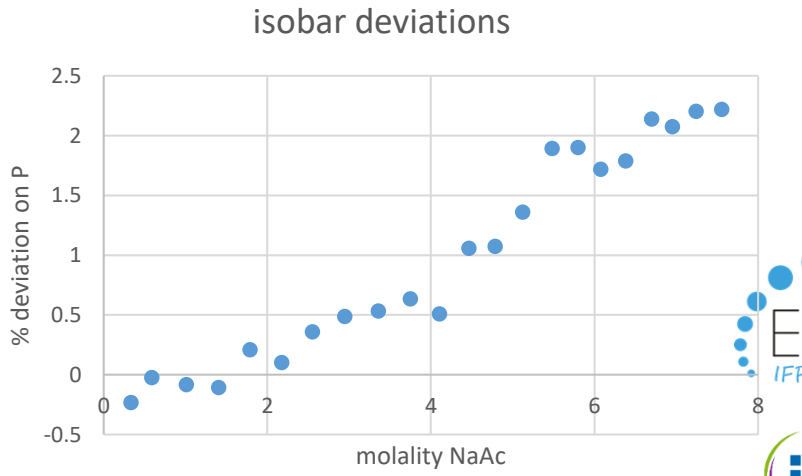


ÉNERGIES NOUVELLES

- New parameters, PD, X6







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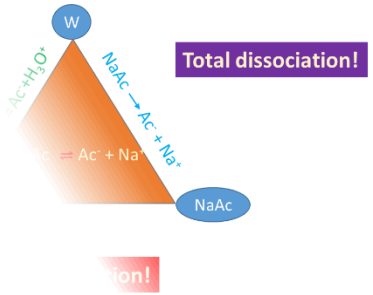
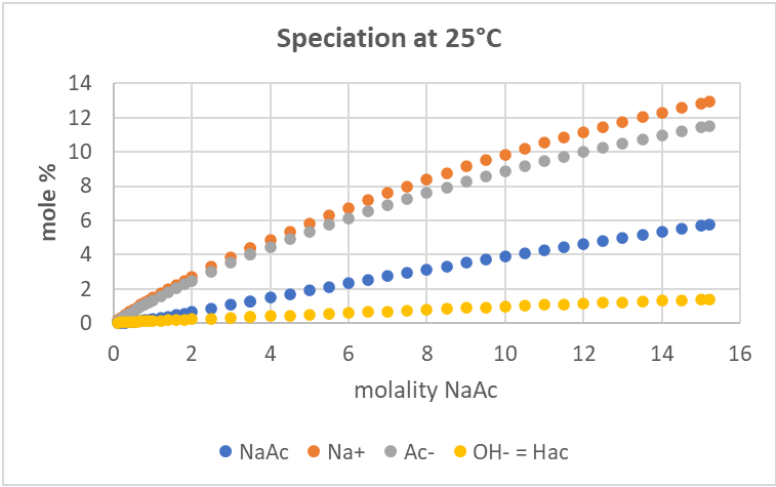
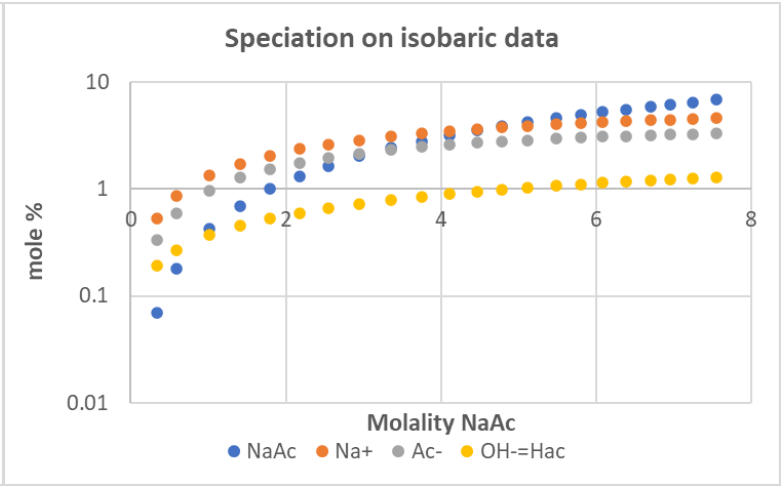
3. BINARY WATER-NAAC

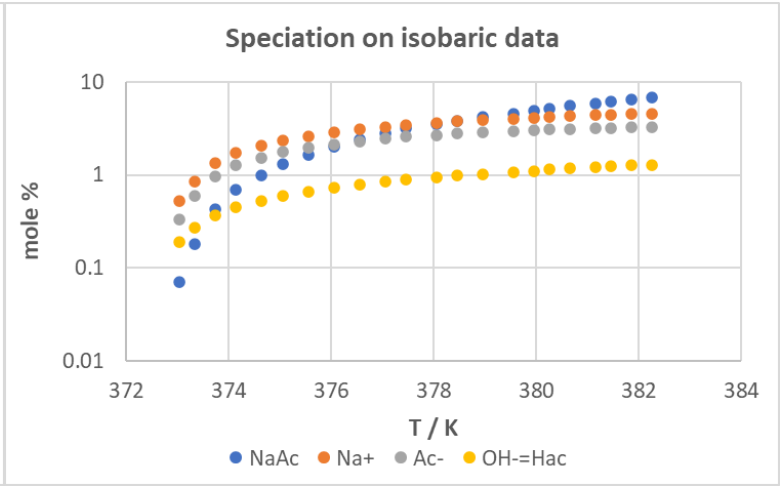


ÉNERGIES NOUVELLES

- New parameters, PD, X6







⇒ Dissociation is strong at low concentration; less so at high concentration
⇒ Dissociation is strong at low temperature; less so at high temperature and high concentration
⇒ This is thanks to large activity coefficient of NaAc (up to 1000)
⇒ Some acetic acid (HAc) is formed together with OH-: it is more stable than Ac- (the solution is basic!)

$$H2O + Ac^- = HAc + OH^-$$

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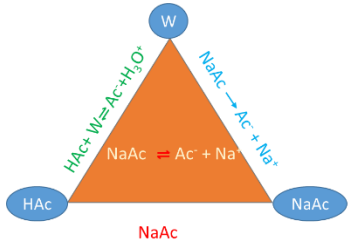
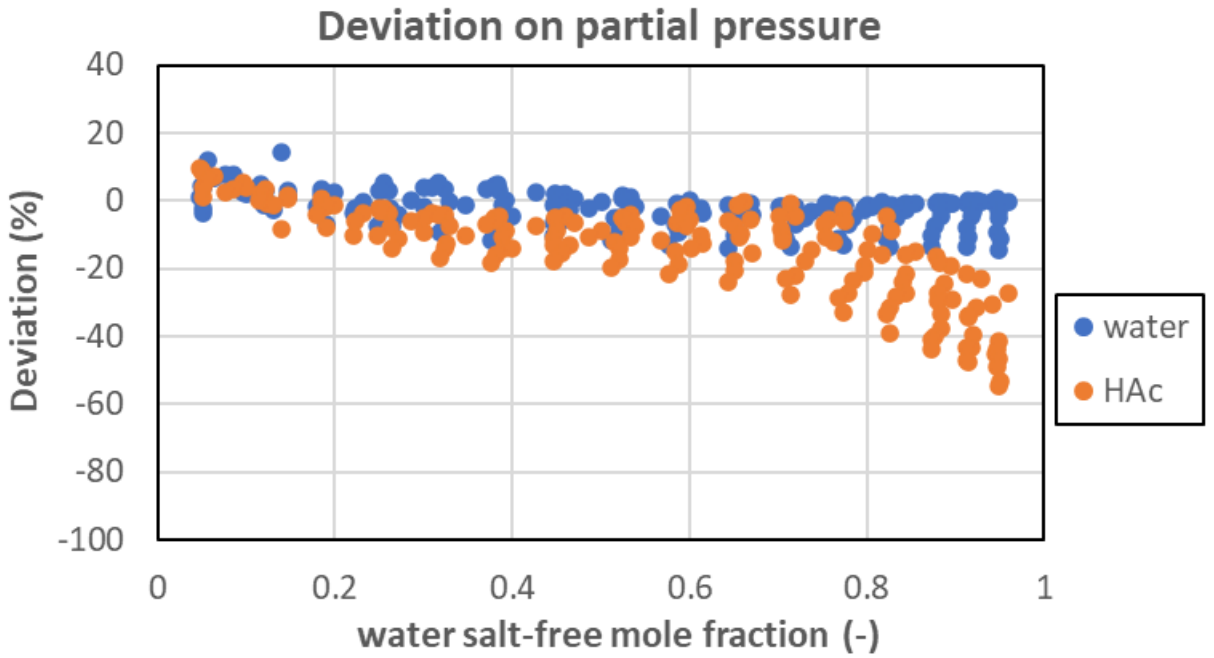
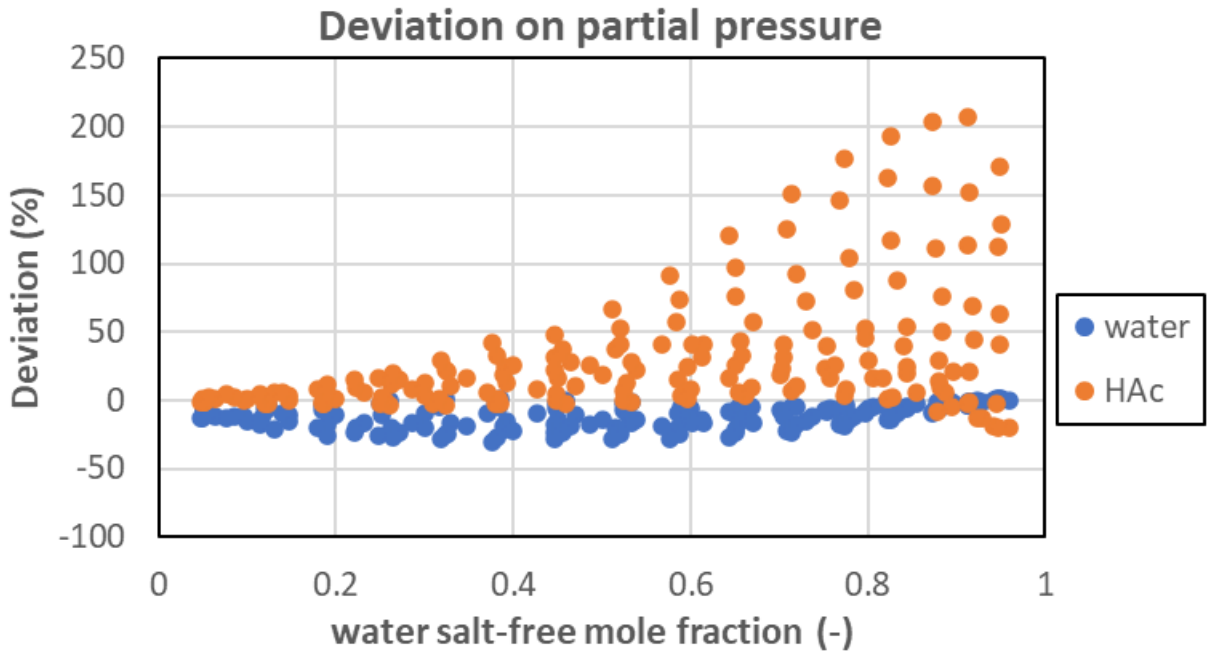
4. TERNARY WATER-HAC-NAAC



Full dissociation



No dissociation



FD: OK for water PP; large deviations for Hac at high water mole fraction

ND: OK when water concentration is small (below 40%); above large deviations

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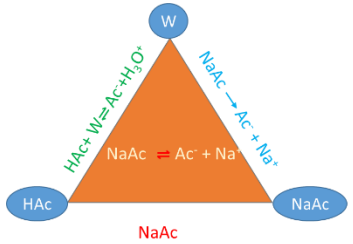
4. TERNARY PD_X8



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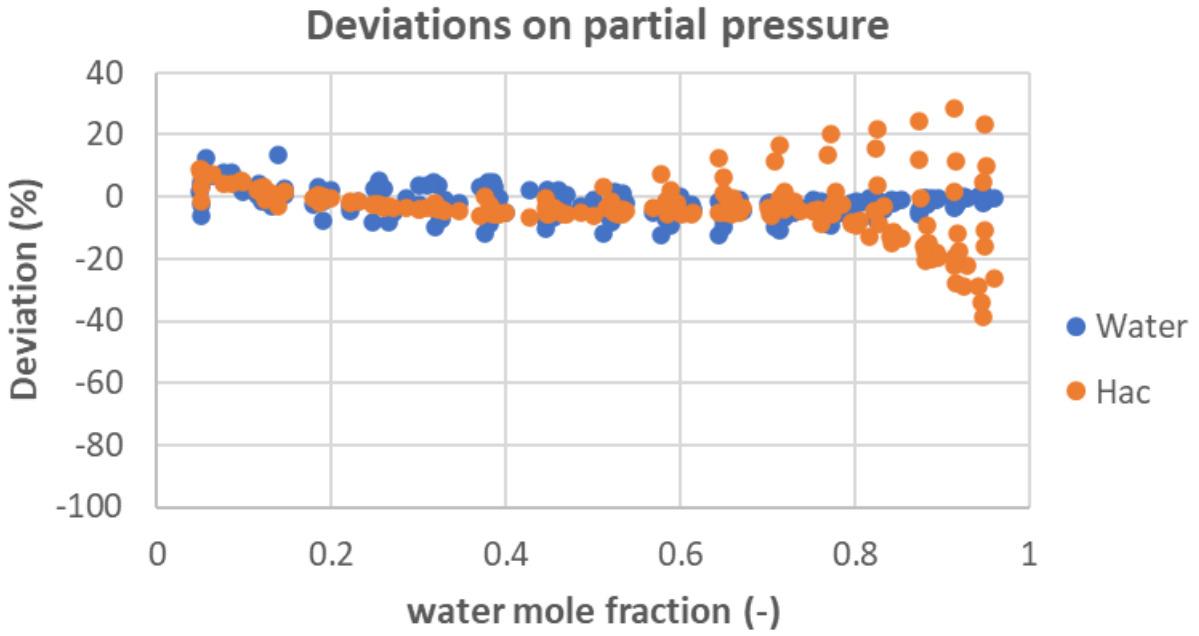

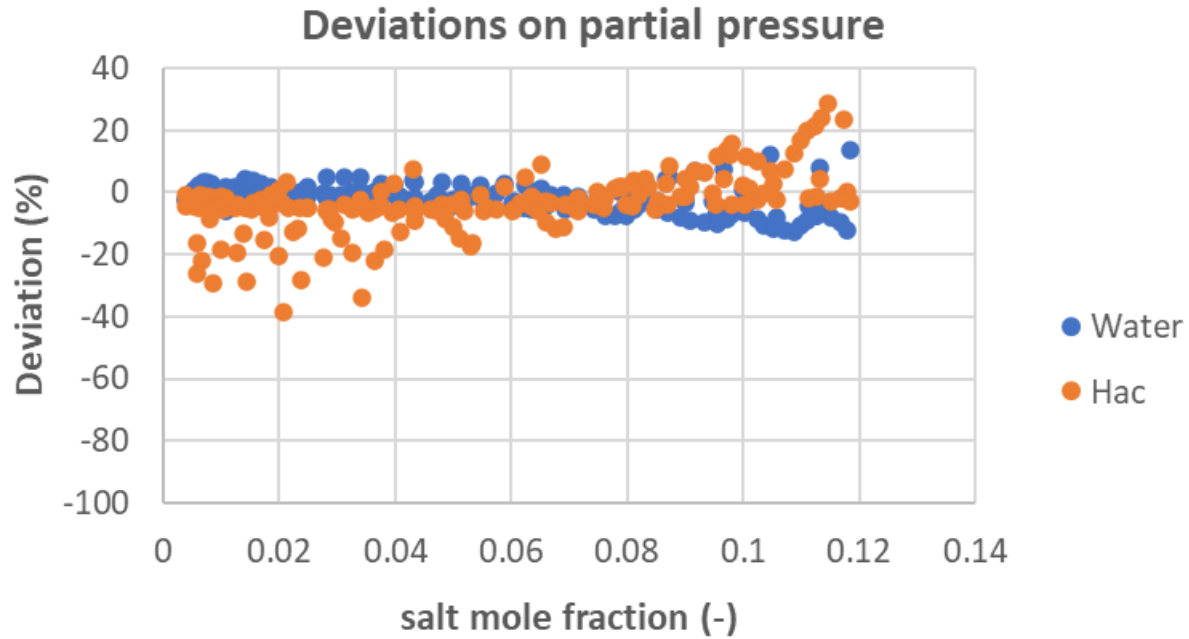

Reasonable deviations with regressed parameters

Highest deviations observed for Hac in high dilution (water mole fraction > 0.8)

At high water concentration:

- Low salt content: negative Hac deviation
- High salt content: positive HAc deviation

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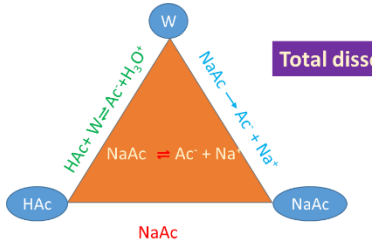
4. TERNARY PD_X8: SPECIATION



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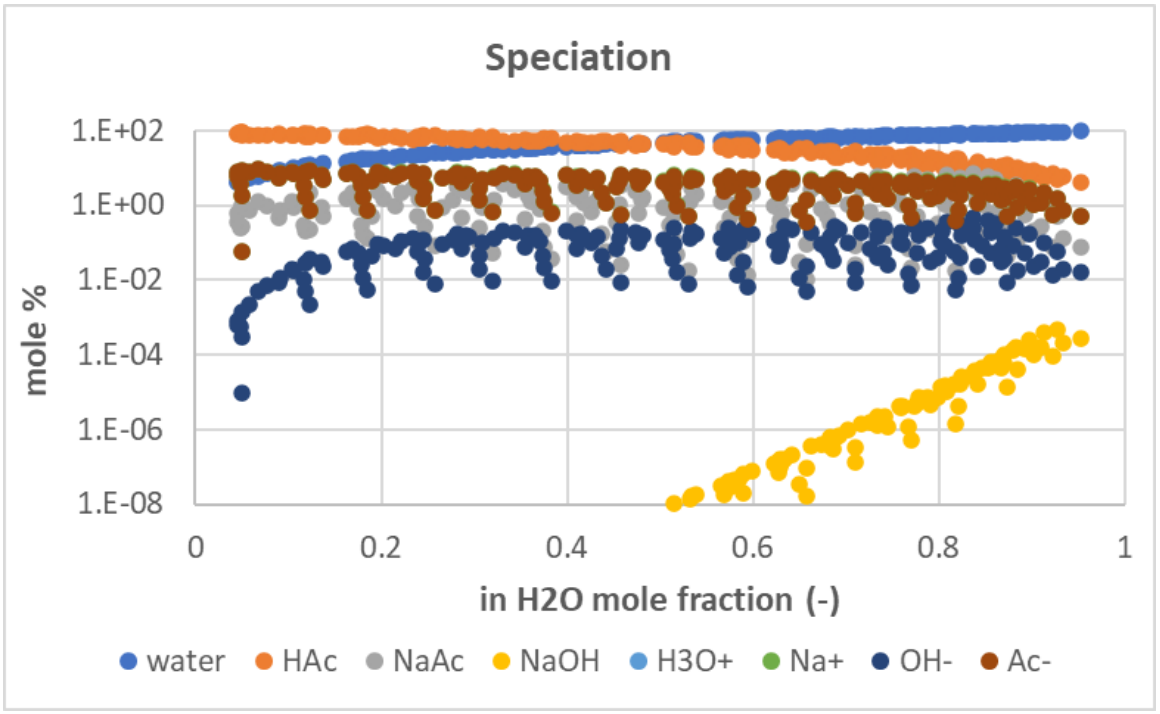

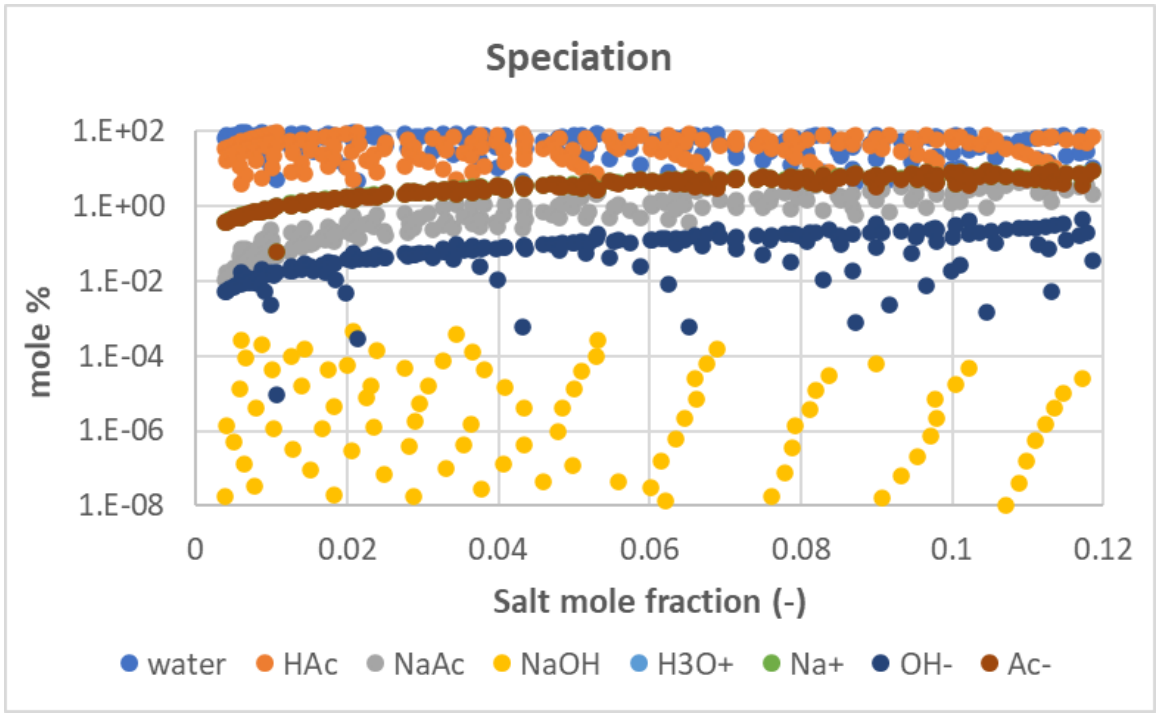

- Majority compounds are generally the ionic species (Na+ = Ac-)
- **Ionic species appear even at very low water content**
- Solution is slightly basic [OH-] ~0.01%
- NaOH is negligible

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NETWORK DISSEMNATION

- Web site
- EFCE Webinar
- ESAT round table discussion
- Publications
  - Vaque-Aura
  - Tsanas et al (reactive fl
  - Yang et al (ERC, submit
- Contribution to an active community:
  - DTU ERC with four academic partners
  - EleTher chair : 2 PhD

Journal of Chemical&Engineering Data

pubs.acs.org/jced Article

Data Analysis for Electrolyte Systems: A Method Illustrated on Alkali Halides in Water

Santiago Vaque Aura, Juan-Sebastian Roa Pinto, Nicolas Ferrando, Jean-Charles de Hemptinne,* Antoon ten Kate, Susanna Kuitunen, Nikolaos Diamantonis, Thomas Gerlach, Manfred Heilig, Gaetan Becker, and Mathias Brehelin

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Calculation of phase and chemical equilibrium for multiple ion-containing phases including stability analysis

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