Ele-Ther :
E-Thermodynamics Joint Industrial Project (JIP)

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User community

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Many new processes involve electrolytic systems that include ionic species and chemical reactions (e.g. biomass; batteries; corrosion; hydrometallurgy; CCUS; …)

Objectives of the project are:

- Create a peer network
- Define case studies inspired by industrial need
- Define best practices (using case studies)
- Promote further research to solve new challenges

Challenge 1:

Availability of Reaction constants ⇔ formation properties

$$\prod_i \left(\frac{f_i}{f_i^0}\right)^{\nu_i} = \exp\left(\frac{-\sum_i \nu_i \mu_i{}^0}{RT}\right) = K$$

Originating from measurements or *ab initio* calculations

Be careful about the reference state

Challenge 2:

Robust reactive algorithms including stability analysis

We recommend global minimization [1] :

$$Gmin = \sum_\phi \sum_i n_i^\phi \mu_i^\phi$$

$$\mu_i^\phi\left(T,P,n_i^\phi\right) = \mu_i{}^0 + RTln\left(\frac{f_i^\phi}{f_i^0}\right)$$

Challenge 3:

Non-ideality model :

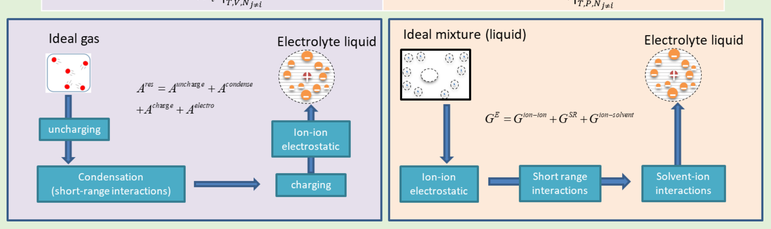
In all cases need for parameters

⇒ **Need for data**

⇒ **Need for an appropriate regression procedure**

Two families of models

Equations of state	Gibbs energy = activity coefficient
$A(T,V,N) = A^{ig} + A^{res}$	$G(T,P,N) = G^{idMix} + G^{E}$
$RT\ln\varphi_i = RT\ln\varphi_i^* \gamma_i = \frac{\partial A^{res}}{\partial N_i}\Big\vert_{T,V,N_{j\neq i}} - RT\ln Z$	$RT\ln\gamma_i = \frac{\partial G^E}{\partial N_i}\Big\vert_{T,P,N_{j\neq i}}$



	E-Eos	Pitzer	MSE	e_NRTL/ eUNIQUAC	SIT
Application fields	General phase equilibrium calculations	Geoscience and chemical industry	Corrosion processes. Oil and gas production (upstream). HPHT conditions	General phase equilibrium calculations; chemical industry.	Coordination chemistry (complex formation)
Advantages	Use of statistical thermodynamic concepts to improve predictivity Capable to describe derivative properties + critical points	Accessible and versatile. Availability of parameter in data base. Valid for ternary systems at high concentrations	Mixed solvents Valid for systems with two potential electrolyte phases (LLE). Includes pressure-dependent parameters	Mixed solvents Flexibility, precise for different conditions Aspen recommended	Simple and pragmatic; only solute volatilities
Disadvantages	Not mature Many different versions	Parameters difficult to determine experimentally. Only pure water solvent	Many parameters, property of OLI	The more binary parameters adjusted, less reliability on the extrapolation	No high concentrations Doesn't comply with Gibbs-Duhem: No solvents
Number of parameters	Variable : aim for physical parameters so as to reduce its number	3 binary parameters + ternary parameters	6 pressure-dependent parameters	5 binary parameters	1 Parameter per ion pair
Principle	Sum of residual Helmholtz energy functions	Interactions based on electrostatic forces and viral expansion	Include a middle-range interaction term instead of Born	Interactions based on the local composition	Linear correction beyond Extended Debye Hückel

Design a case study that focuses on the fluid phase properties.

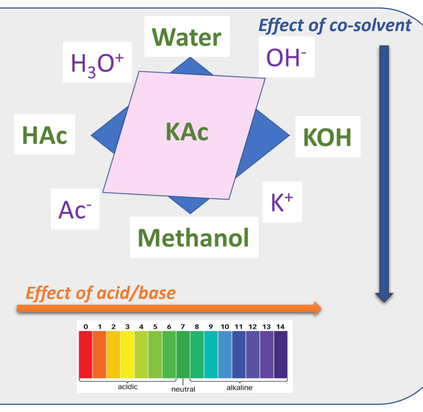
A four-component system is selected:

- Water and a co-solvent (because in practice pure aqueous solutions are rare)
- An acid and a base (ideally one of them is weak): such system is used to buffer a solution

We focus on **VLE & LLE** (volatilities ; salting in/salting out effects)

In practice, because of the reactions the four components system may become a nine components system thus complexifying the parameterization

No data for such quaternary system could be found in the literature



Best practices: 1. Data analysis

= Evaluate trends

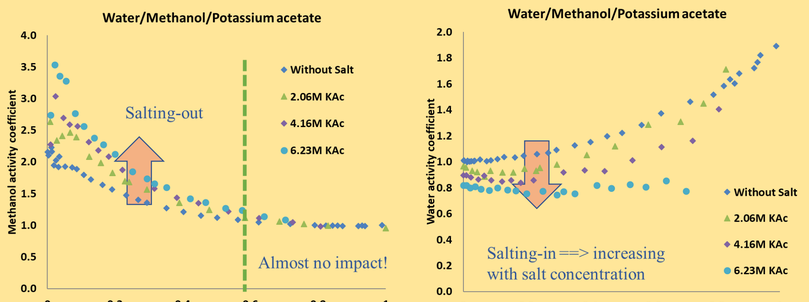
Data collection

➔Internal consistency: **check validity of data according to thermodynamic principles**

➔External consistency: **evaluate trends comparing families of systems**

Ex: ternaries PTxy data => plot the experimental solvent activity coefficients using $\gamma_i = \frac{y_i \times P}{x_i \times P_i^\sigma}$

The plot clearly shows the salting in and salting out effects [2,3]

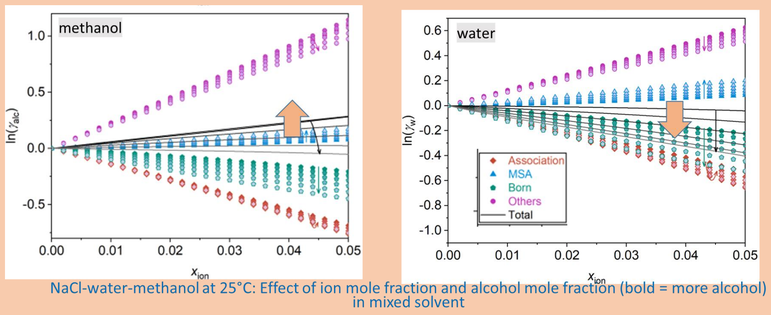


Best practices: 2. Data extrapolation (to process conditions)

= Identify a method that can replicate the trends (predictive modeling)

Advanced tools for validation & extrapolation

Ex: e-PPC-SAFT [4] =>
The effect of salt on the solvent activity coefficients is a measure of the salting out (when log is positive)
or salting in (when log is negative)



NaCl-water-methanol at 25°C: Effect of ion mole fraction and alcohol mole fraction (bold = more alcohol) in mixed solvent

Best practices: 3. Industrial Model Calibration

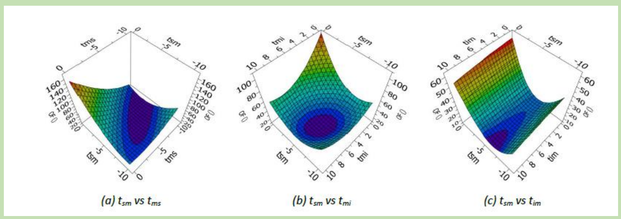
Correlative models calibration

Setup assumptions for the modelling :

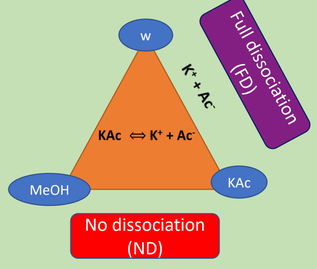
- Choice of the model (here e-NRTL), dissociation scheme (here we checked full dissociation of the salt, partial and no dissociation),…
- Select the data and objective function (here Partial Pressures)
- Identify the parameters to be adjusted (here $\tau_{solvent\text{-}salt}$ from eNRTL) and those that can be set to some predefined values

➔use sensitivity analysis

the objective function is insensitive to the parameter along the valley axis



Example with Water – KAc – Methanol ternary



The full system contains both ion-pairs (KAc) and ionic species (K^+ and Ac^-) => it must be described with **Partial dissociation (PD)**

Proposed fitting approach

1. τ_{ws}/ τ_{sw} from Aspen kept unchanged
2. **τ_{wi}/ τ_{iw}** fit on bin data (W+KAc)
3. τ_{ms}/ τ_{sm} & τ_{mi}/ τ_{im} fit on (MeOH + KAc) bin and/or ter data

$\mathbf{w}$: $water$
$\mathbf{m}$: $methanol$
$\mathbf{i}$: $ions(K^+, Ac^-)$
$\mathbf{s}$: $salt(KAc)$

Parameter set	Binary M+KAc PD	Ternary Data only PD	Binary +Ternary Data PD
	AAD%	AAD%	AAD%
MSI_2	1.34	**17.94**	**17.42**
MSI_3	1.36	**18.29**	**17.77**

Several (here two : MSI_2 & MSI_3) equivalent parameter sets can be found

In the absence of speciation data, the only way to distinguish them is to evaluate their quality by:
- using ND hypothesis on binary system with methanol
- using FD hypothesis on binary system with water

This is a consequence of the different speciation that results from the different parameter sets

➔ Choice of parameter set

Parameter set	Binary M+KAc ND
	AAD%
MSI_2	**1.48**
MSI_3	7.62

Conclusions and Perspectives

1. EleTher JIP aims at creating an industrial network of electrolyte thermodynamics
2. Objective is to investigate a quaternary systems including mixed solvents and both weak and strong electrolytic species
3. Best practices for developing industrial models are based on three steps: data analysis - extrapolation using a physical approach – model calibration
4. Further work to be performed on another case study / another modeling approach
5. For academic research: investigate the link between salting in/out and speciation

References

1. Tsanas et al: « Calculation of phase and chemical equilibrium for multiple ion-containing phases including stability analysis" 2021, Chem. Eng. Sci., 248A, 117174
2. 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
3. Yang, F et al. : « A Benchmark database for mixed solvent electrolyte solutions: consistency analysis using e-NRTL » 2022, I&EC Research, 61, 15576-15593
4. Yang, F. et al: Composition-dependence of relative static permittivity in ePPC-SAFT for mixed-solvent alkali halides, 2023, submitted to Fluid Phase Eq.