MODÈLES THERMODYNAMIQUES POUR LA PRISE EN COMPTE DE LA SPÉCIATION DES ÉLECTROLYTES EN PHASE LIQUIDE EN SOLVANT MIXTE

EleTher
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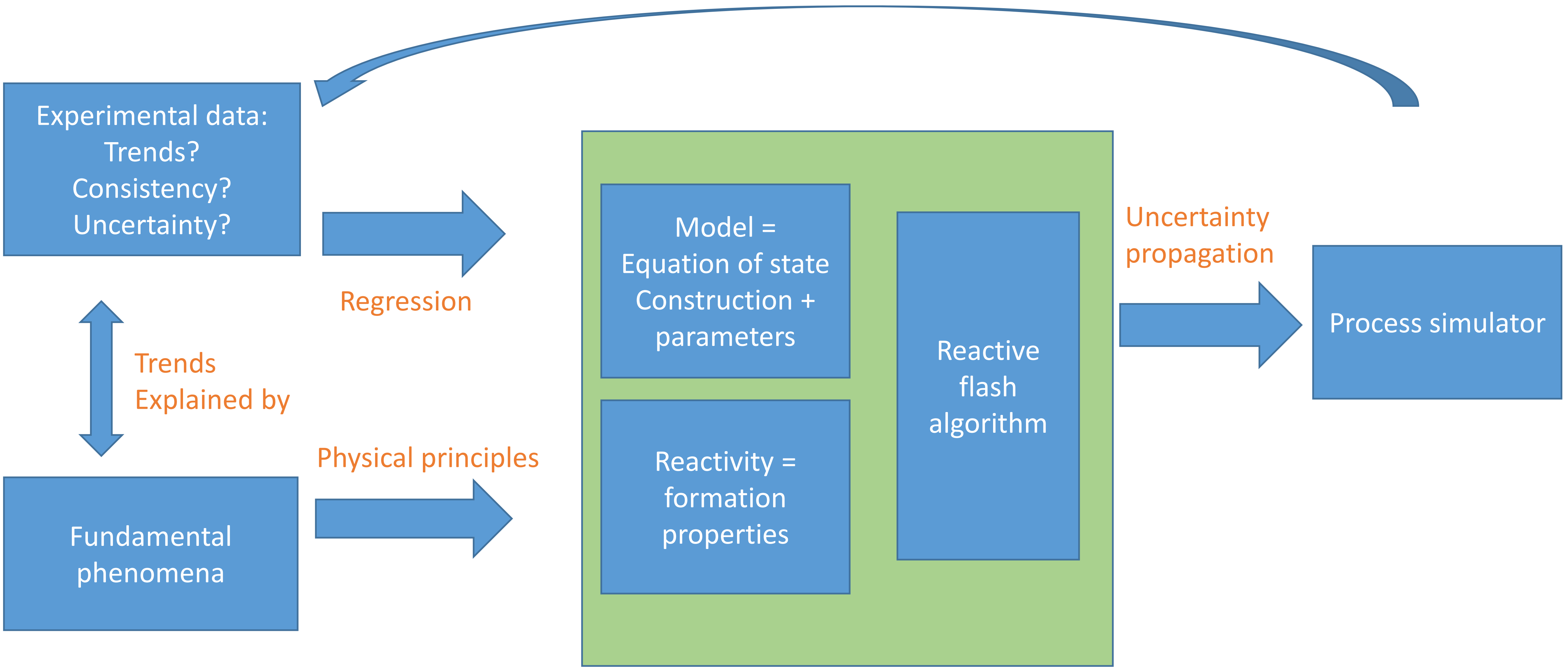
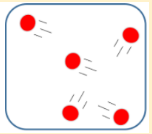
ELETHER CHAIR ROADMAP



CONSTRUCT THERMODYNAMIC MODELS

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

Ideal gas



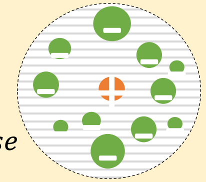
uncharging

Condensation (short-range interactions)

charging

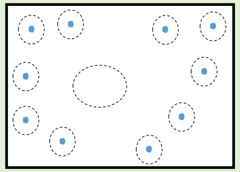
Ion-ion electrostatic

Electrolyte liquid



$$A^{res} = A^{\text{uncharge}} + A^{condense} + A^{\text{charge}} + A^{electro}$$

Ideal mixture (liquid)



Ion-ion electrostatic

Short range interactions

Solvent-ion interactions

Electrolyte liquid

$$G^{E} = G^{ion-ion} + G^{SR} + G^{ion-solvent}$$

CONSTRUCTION OF ION-PAIRING MODEL

Primitive models : Long-range electrostatic interactions between ions(A^{MSA}) + Born (solvation)

Polar interactio

Van der Waals forces

ePPC-SAFT

$$A^{res} = A^{hc} + A^{disp} + A^{assoc} + A^{MAL} + A^{polar} + A^{elec} + A^{Born}$$

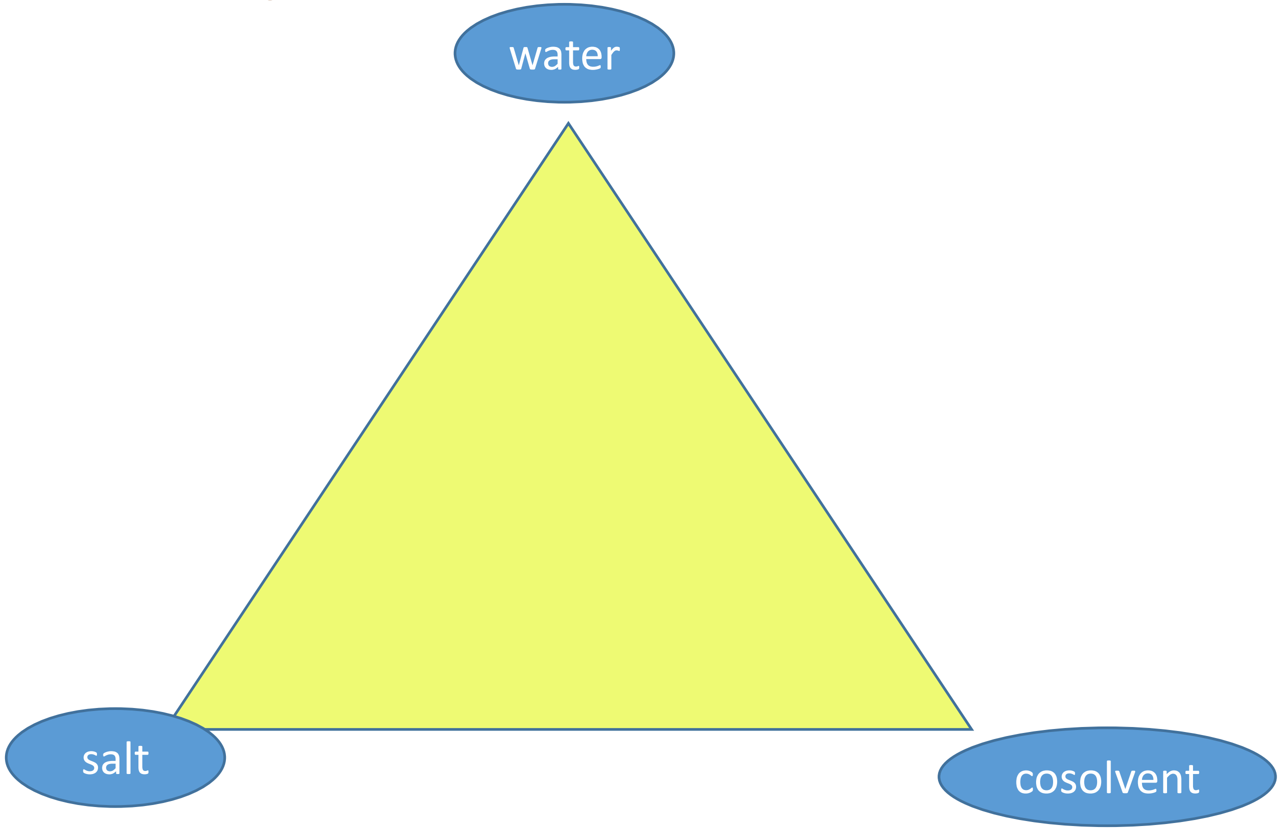
Repulsion

Solvent-solvent + solvent-ion

Ion-pairing

PROPERTIES

- Hydrometallurgical Processes:
- **System :**



F. Ferella et al. / Resources, Conservation and Recycling 108 (2016) 10–20

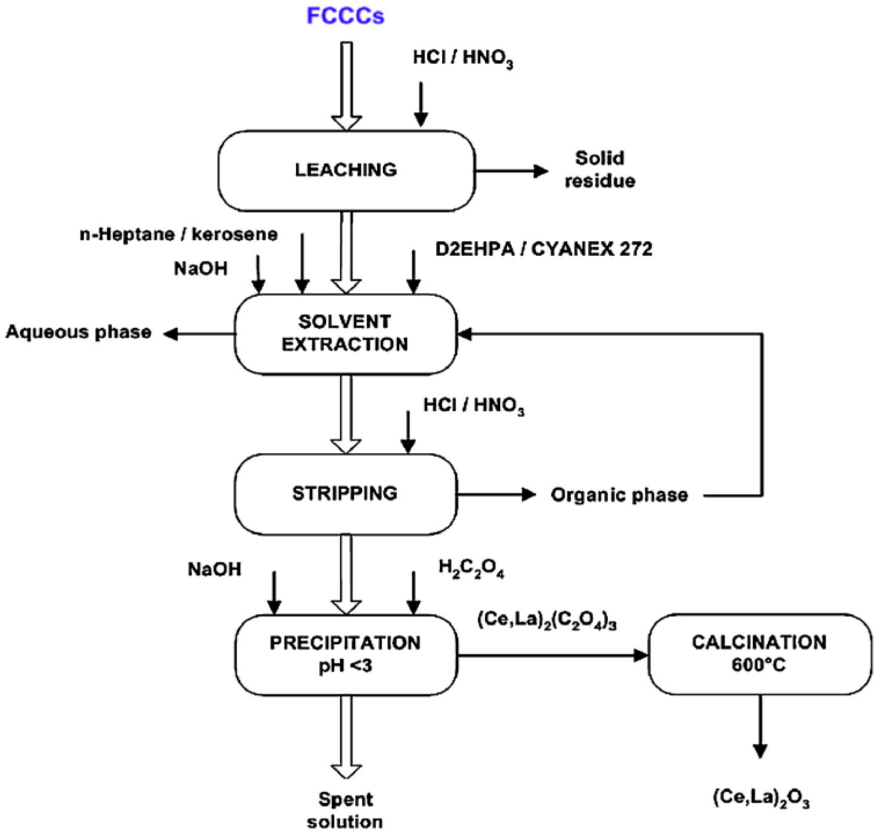


Fig. 3. Flow-sheet of the process described in the Italian patent No. RM2012A000374.

Properties / phases:

VLE

speciation

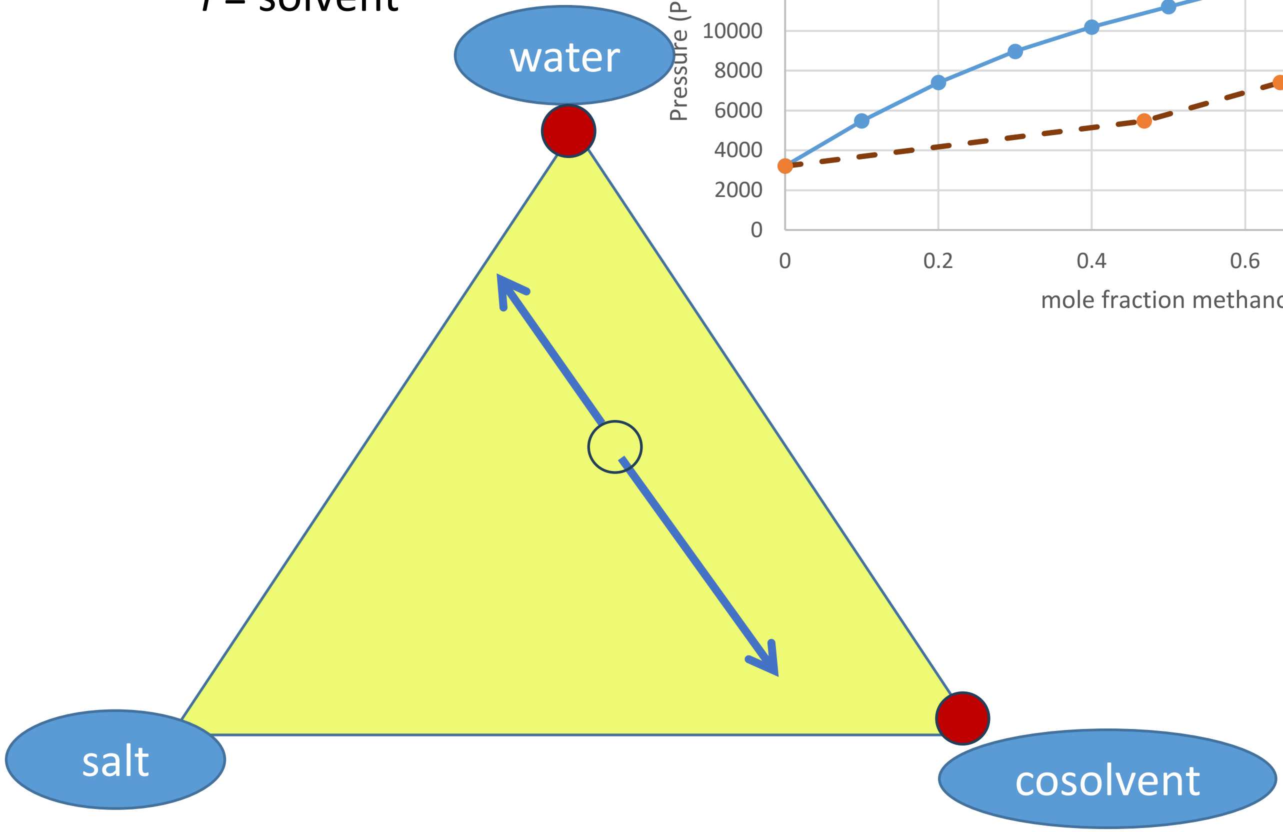
SLE

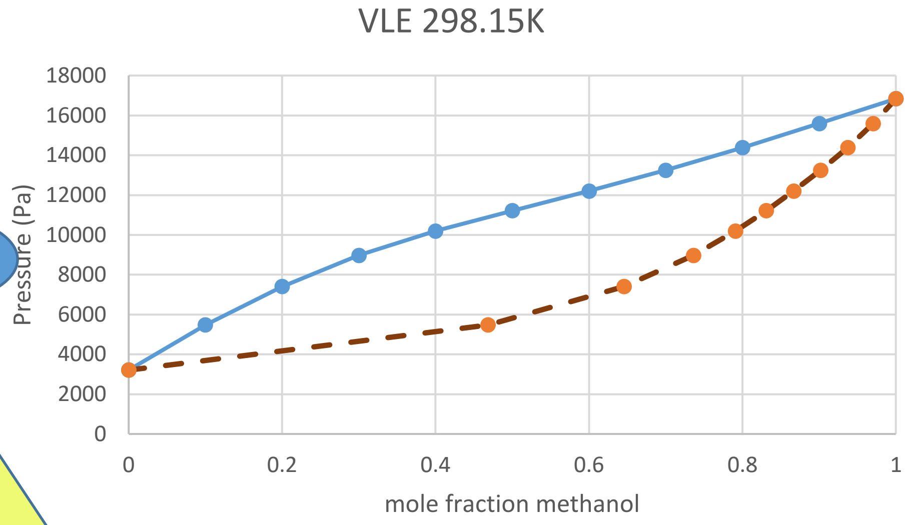
LLE

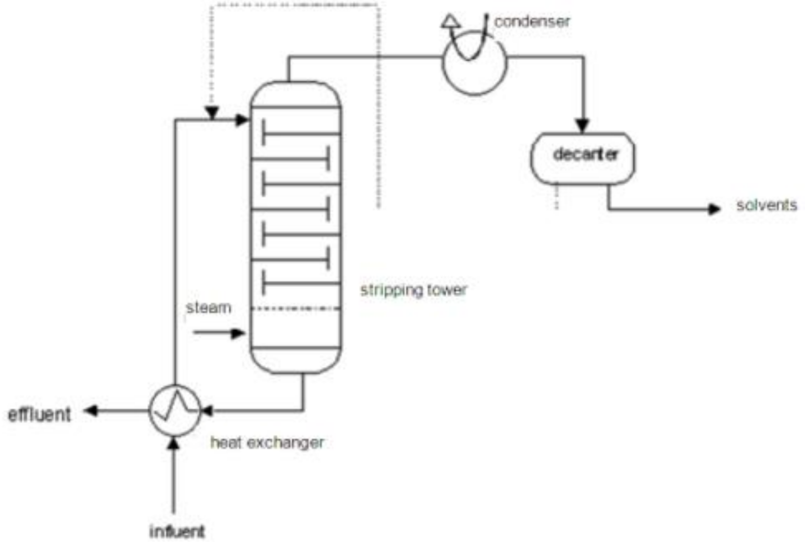
VLE

$$RT ln(\gamma_i) = \mu_i - \mu_i^{ref}$$

i = solvent





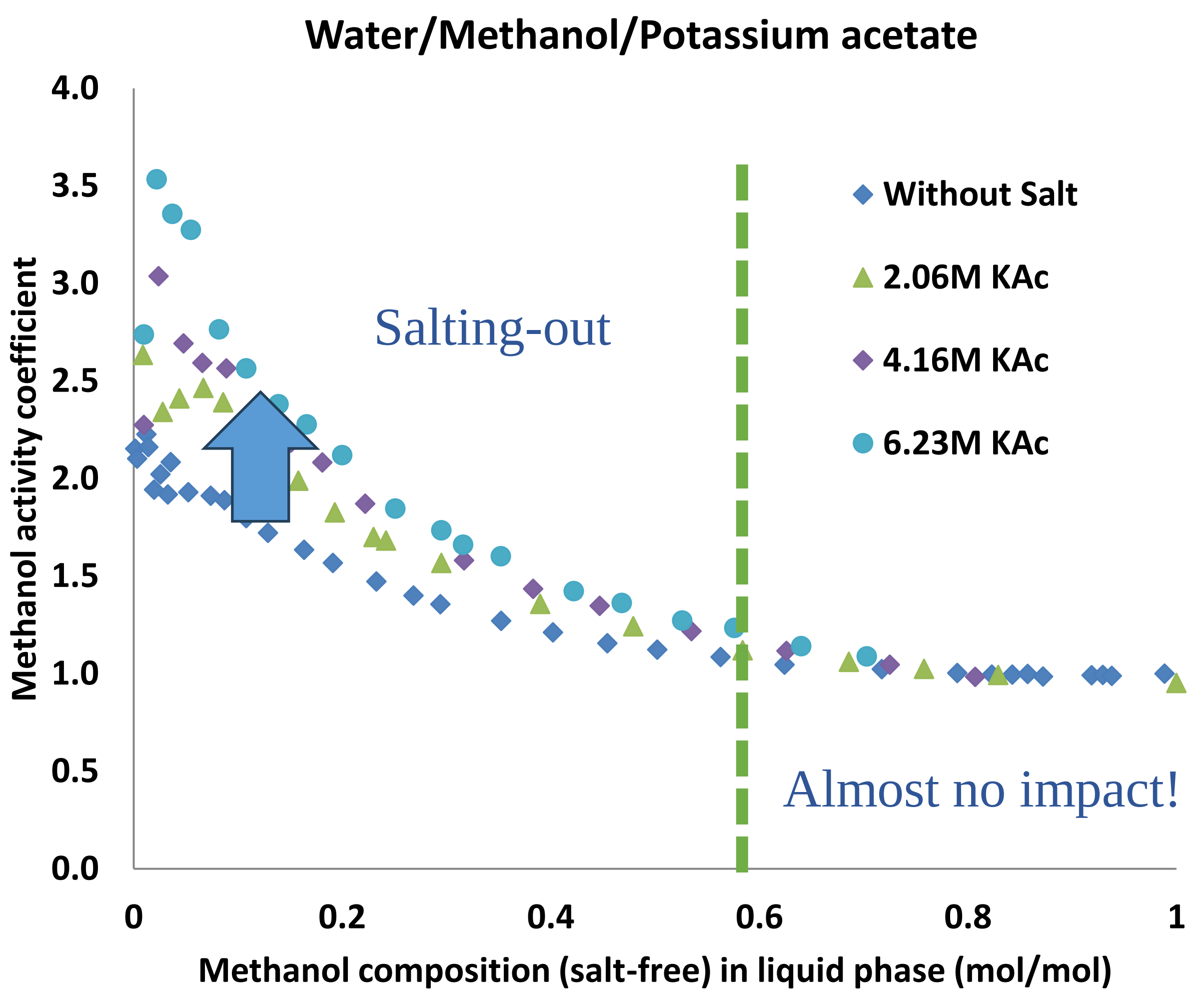


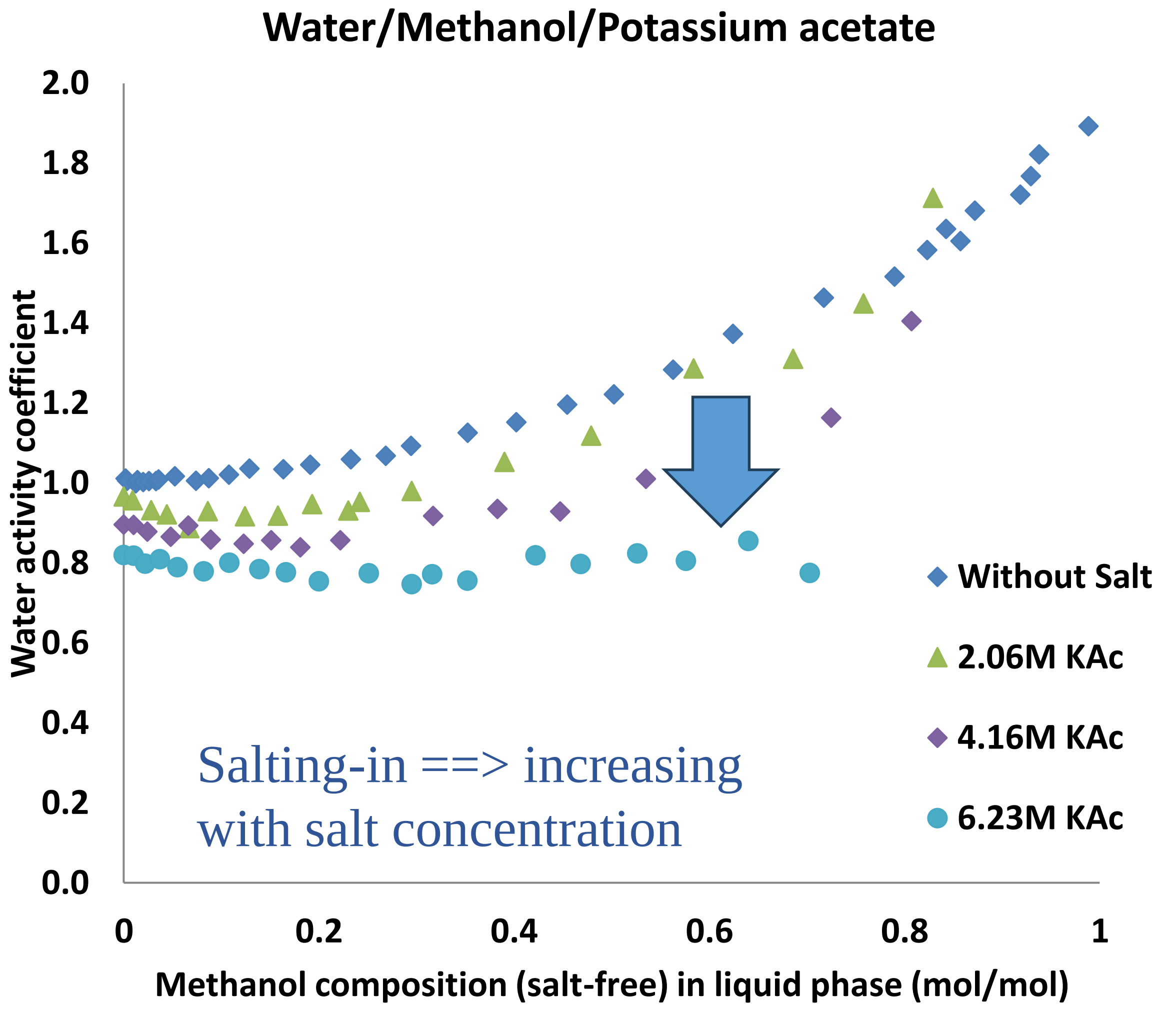
The activity coefficients are an indication of non-idealities

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

$$RT \ln \gamma_i = \sum \left(\frac{\partial A^{res}}{\partial N_i}\bigg|_{T,V,N_{j \neq i}} - \frac{\partial A^{res}}{\partial N_i}\bigg|_{T,V,N_{j \neq i}}^{ref} \right) - RT \ln \frac{v}{v^{ref}}$$

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



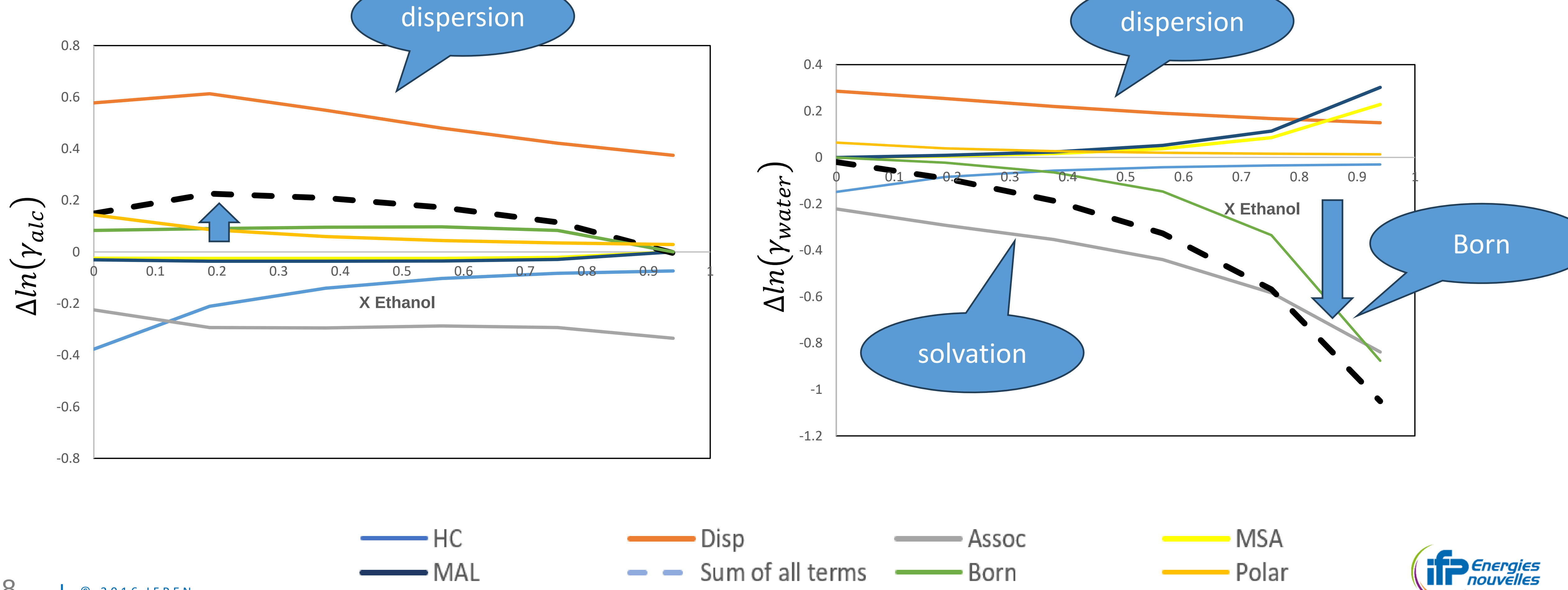


CONTRIBUTION TO THE SALTING-IN/SALTING-OUT EFFECT

$$ln\left(\gamma_i^{x=0.03,s}\right) - ln\left(\gamma_i^{x=0.,s}\right) = \sum\left(\left.\frac{\partial A^{res}}{\partial N_i}\right|_{T,V,N_{j\neq i}}^{x=0.03} - \left.\frac{\partial A^{res}}{\partial N_i}\right|_{T,V,N_{j\neq i}}^{x=0,s}\right) - RT\ln\frac{v^{x=0.03}}{v^{x=0,s}}$$

i = solvent

298.15K



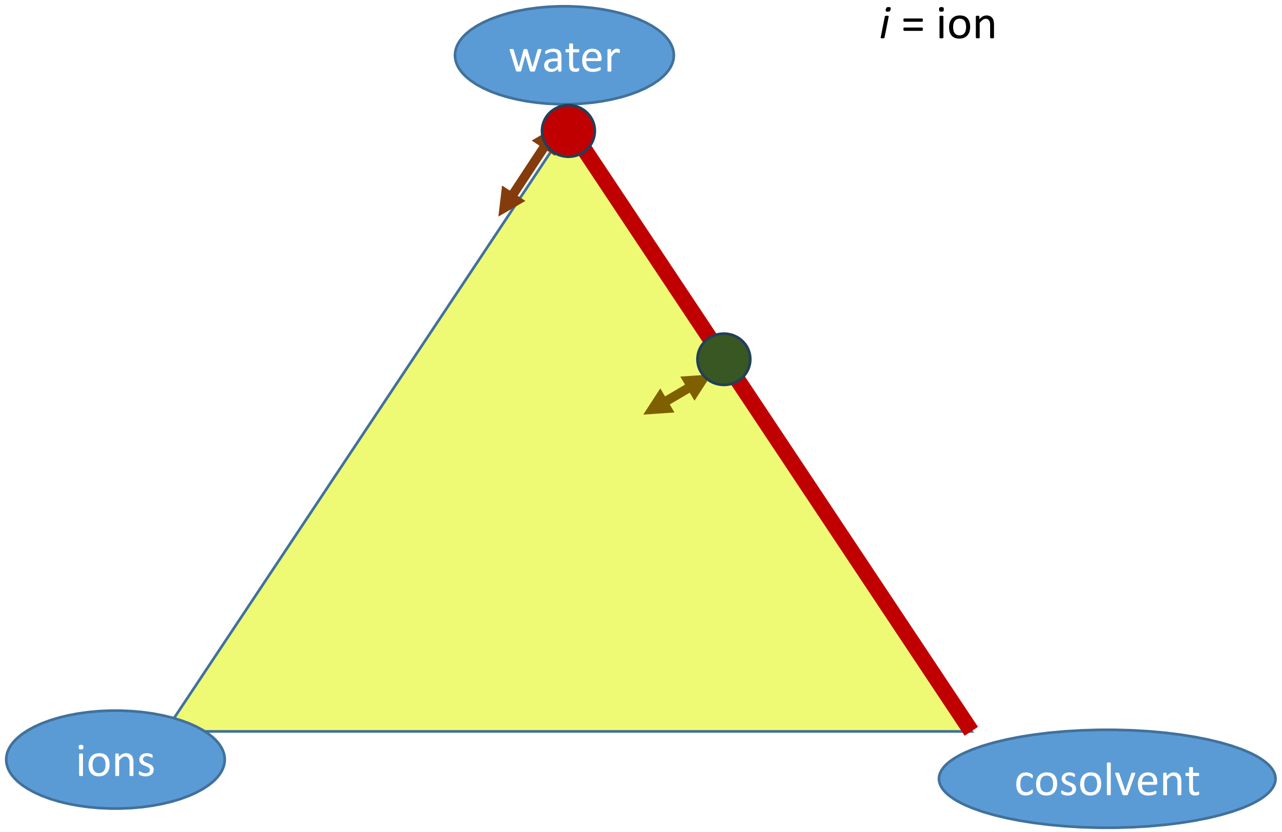
SPECIATION

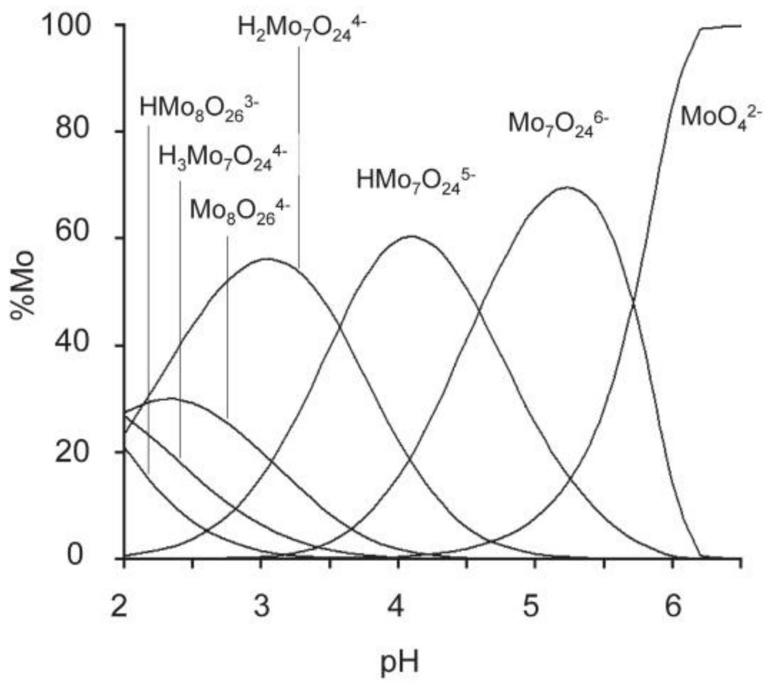
Activity coefficient of the solutes at infinite dilution in the solvent

Gibbs energy of tranfer:

$$RT\,ln(\gamma_i^{*,s}) = \mu_i^{s,0} - \mu_i^{0}$$

i = ion





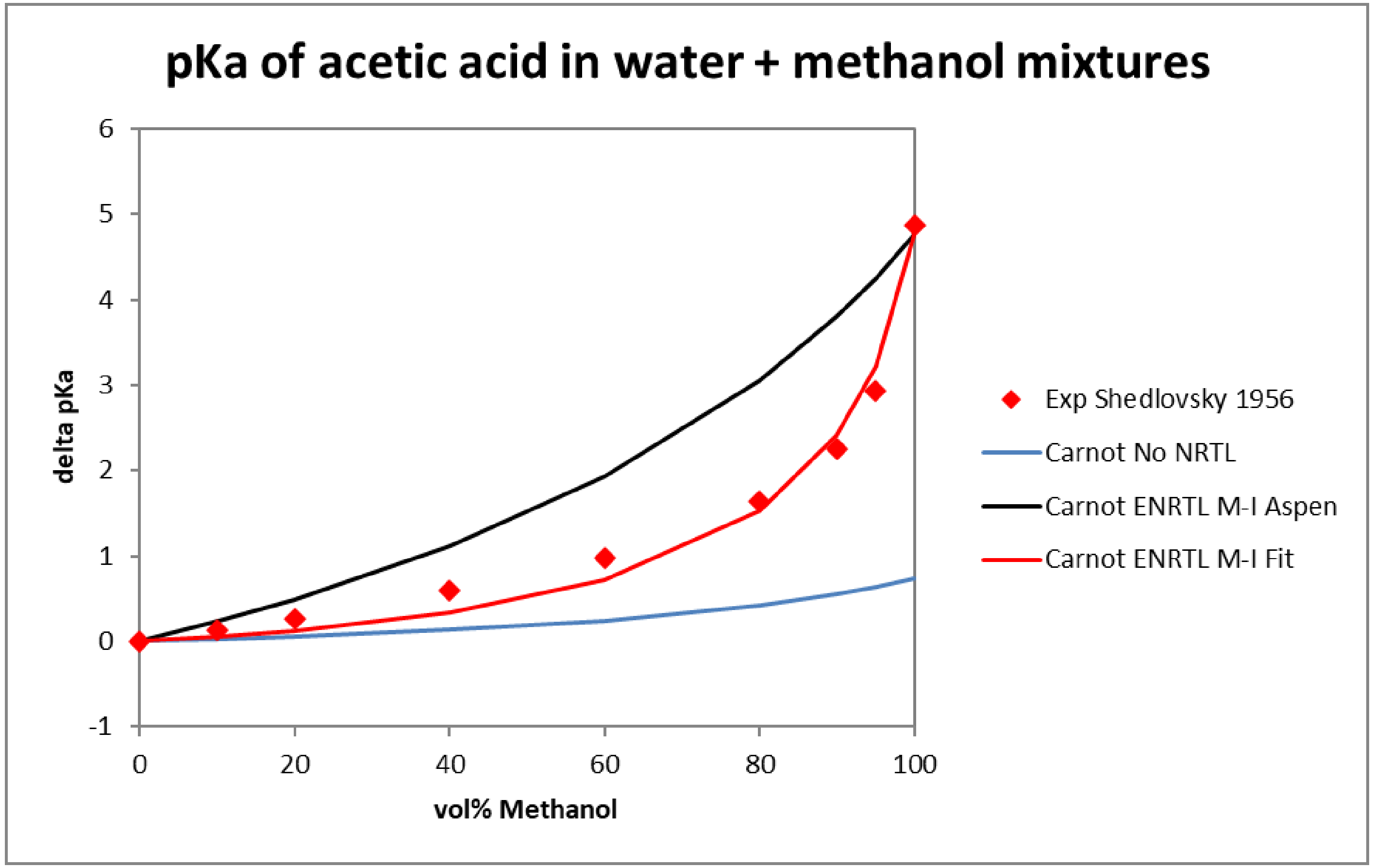
Reaction equilibrium

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

$$ln(K^s) - ln(K) = \frac{-\sum_i \nu_i(\mu_i^{s,0} - \mu_i^{0})}{RT}$$

$$= \prod \left(\frac{f_i^{s,0}}{f_i^{0}}\right)^{\nu_i} = \prod (\gamma_i^{*,s})^{\nu_i}$$

IMPACT OF REFERENCE STATE ON THE EQUILIBRIUM CONSTANT

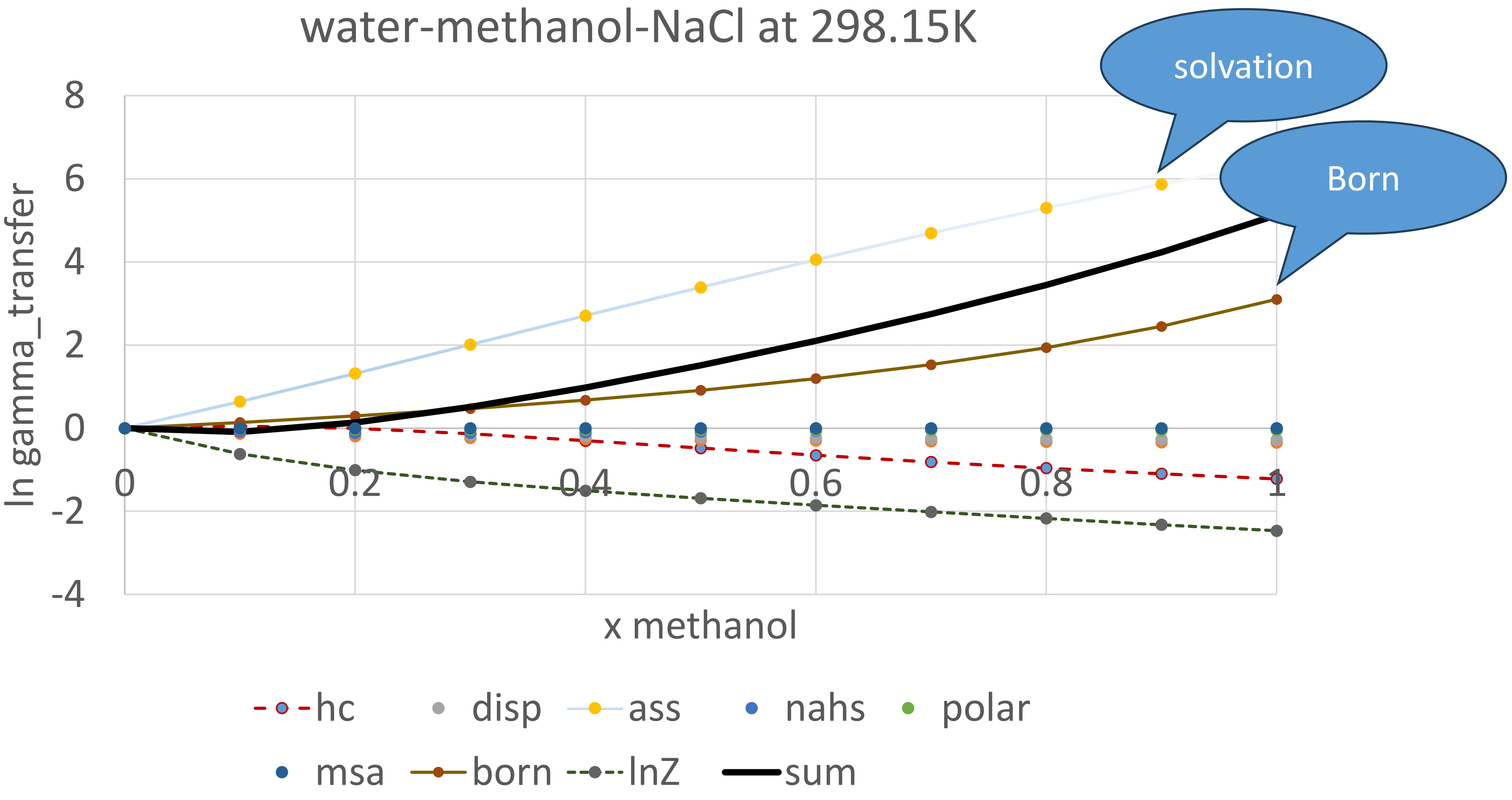


Difference between pKa values, with different model parameters, compared with the data from T. Shedlovsky, R.L. Kay, J. Phys. Chem. 60 (1956) 151–155

GIBBS ENERGY OF TRANSFER (NOT INCLUDED IN REGRESSION)

$$ln\left(\gamma_i^{*,S}\right) = \sum\left(\left.\frac{\partial A^{res}}{\partial N_i}\right|_{T,V,N_{j\neq i}}^{x=0.,s} - \left.\frac{\partial A^{res}}{\partial N_i}\right|_{T,V,N_{j\neq i}}^{x=0,w}\right) - RT\ln\frac{v^{x=0.,s}}{v^{x=0,w}}$$

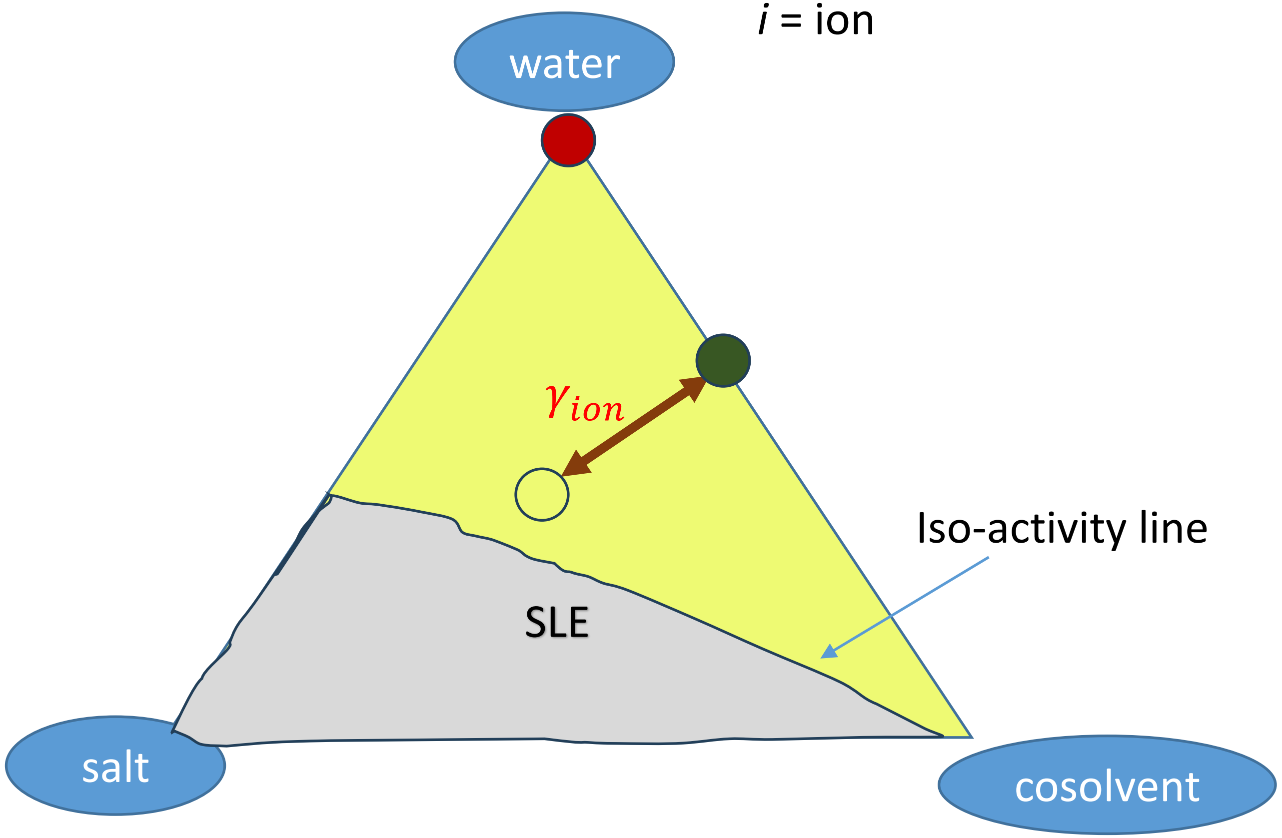
i = ion



SLE (LIXIVIATION; PRECIPITATION)

$$RT\ln(\gamma_{ion}) = \mu_i - \mu_i^{id,0}$$

i = ion



SLE

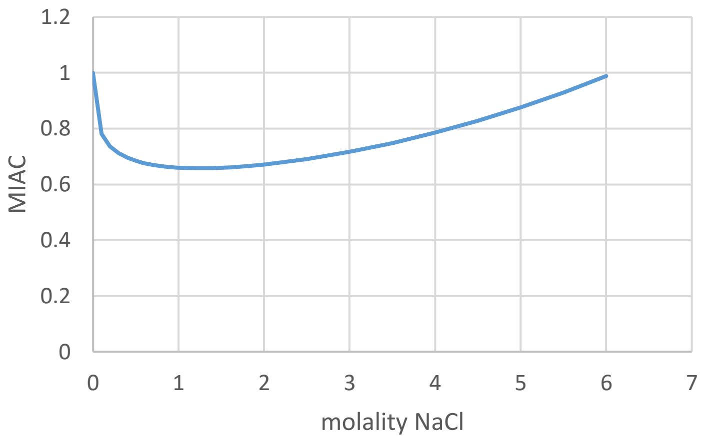
$$\left(x_{B^+_{aq}}\gamma_{B^+_{aq}}\right)^{\nu_A}\left(x_{B^-_{aq}}\gamma_{B^-_{aq}}\right)^{\nu_B} = K = exp^{\frac{\mu_{AB}}{RT}}$$

If activity coefficient is defined in mixed solvent

$$K^s = K\prod\left(\gamma_i^{*,s}\right)^{\nu_i}$$

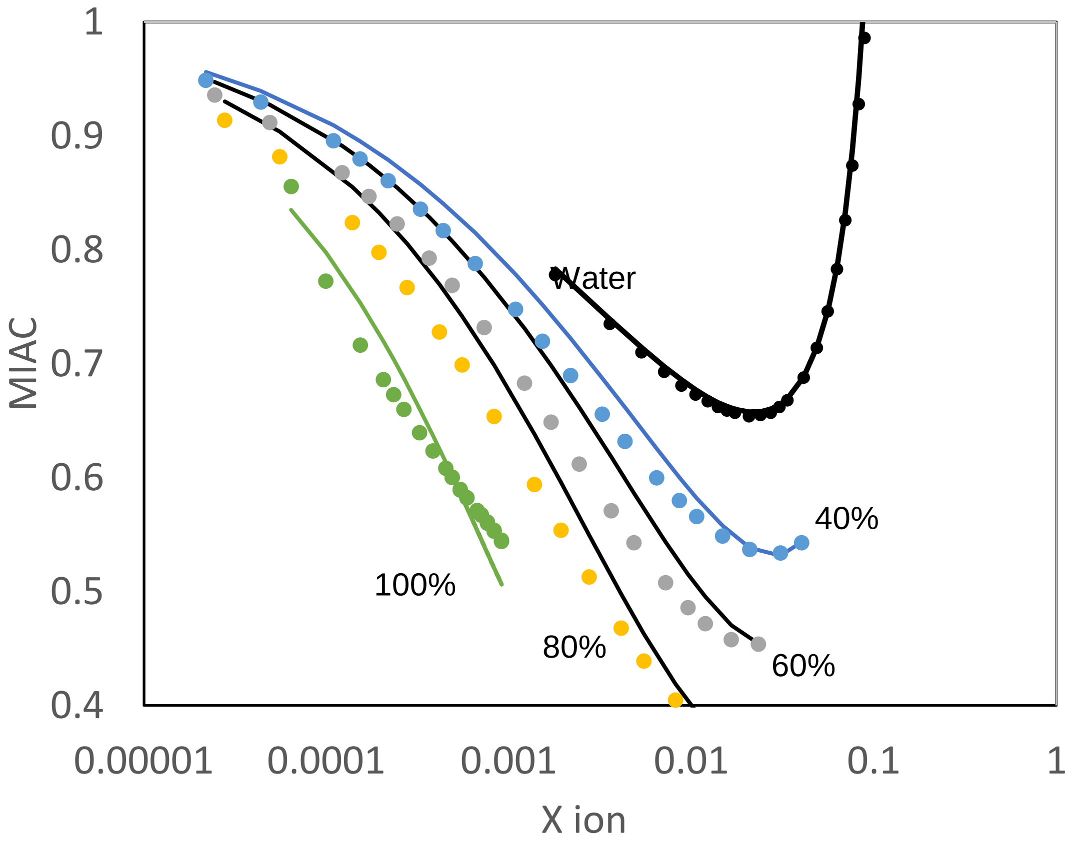
MIAC : from potentiometry

$$RT\ln(\gamma_{+/-}) = \mu_i - \mu_i^{id,s}$$

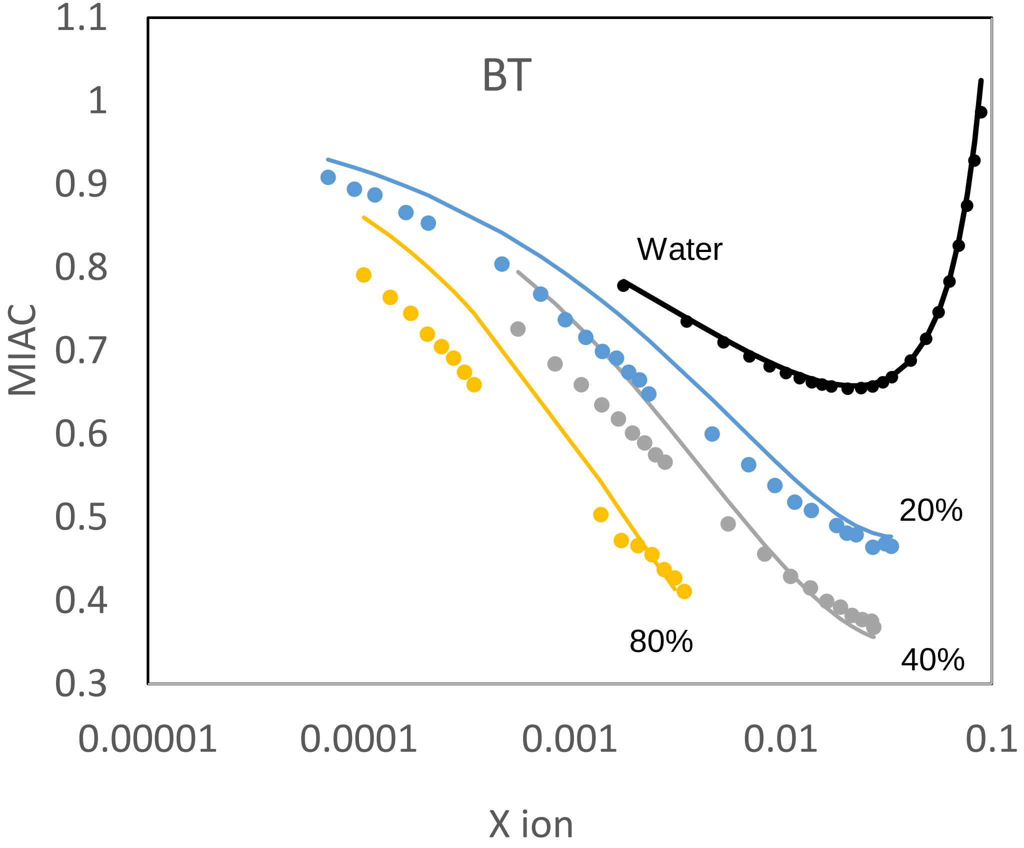


MIAC CONTRIBUTIONS

Water +Methanol +NaCl



Water +Ethanol +NaCl

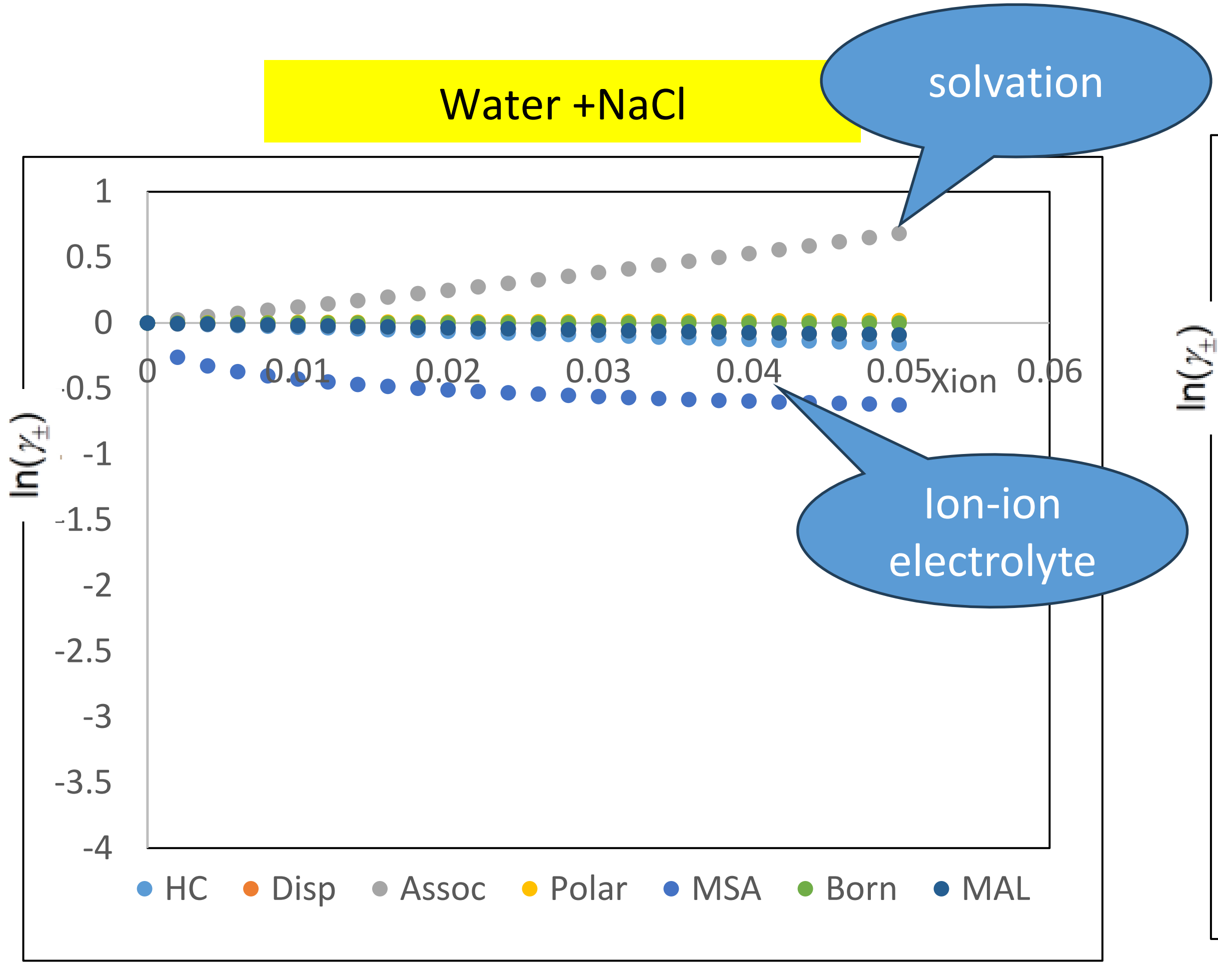


MIAC CONTRIBUTIONS

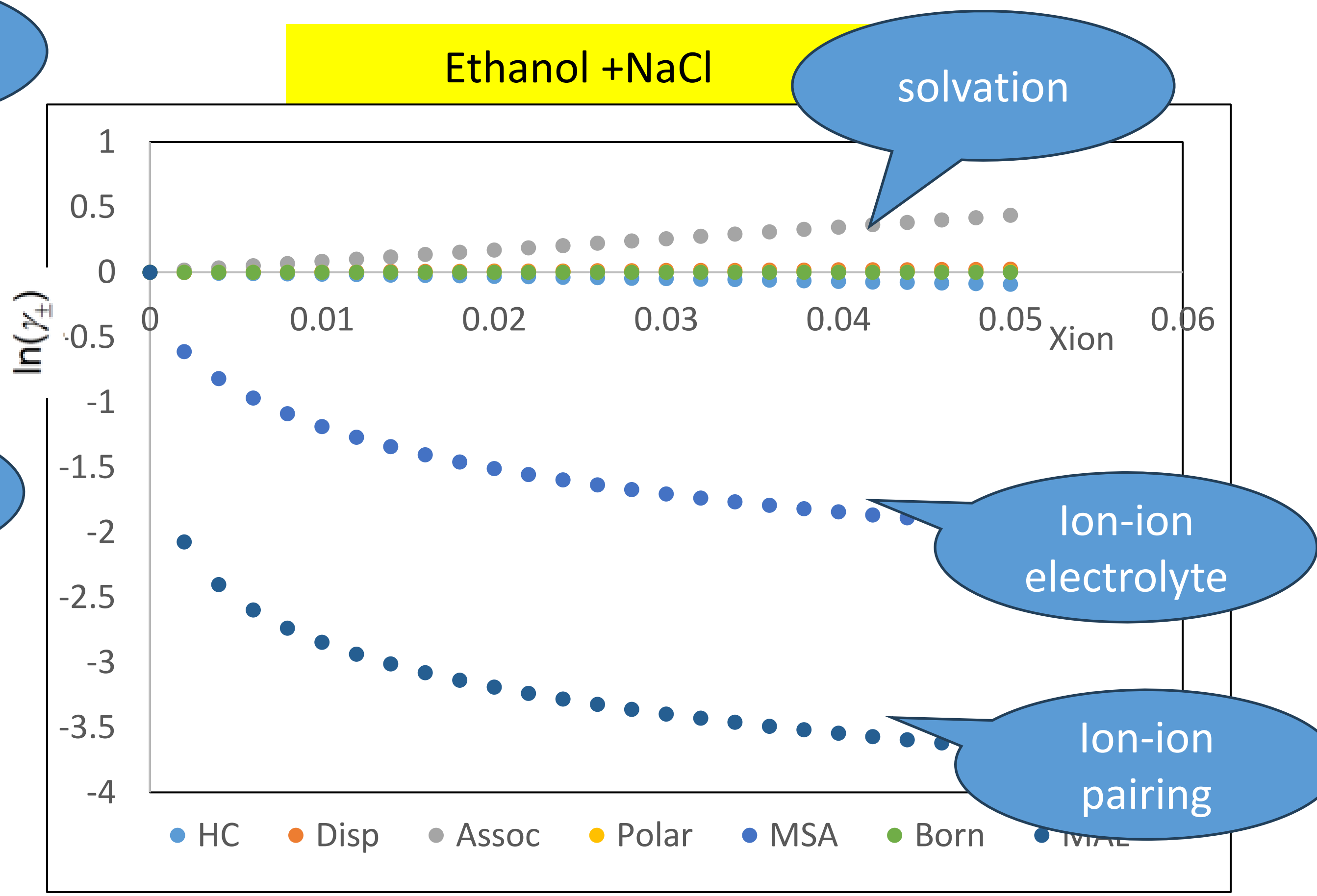
$$ln(\gamma_\pm) = \sum\left(\frac{\partial A^{res}}{\partial N_i}\bigg|_{T,V,N_{j\neq i}}^{s} - \frac{\partial A^{res}}{\partial N_i}\bigg|_{T,V,N_{j\neq i}}^{x=0,s}\right) - RT\ln\frac{v^s}{v^{x=0,s}}$$

i = ion

Water +NaCl



Ethanol +NaCl

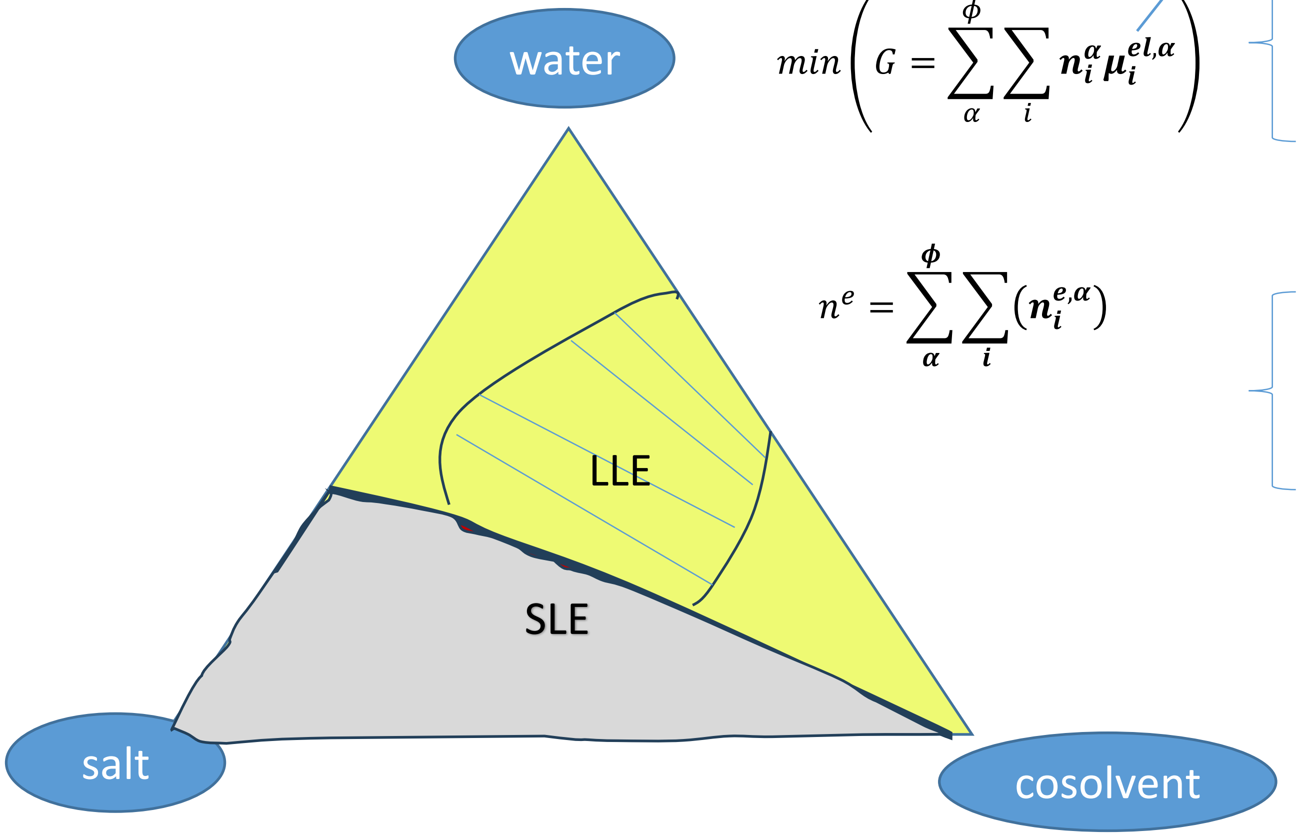


LLE (EXTRACTION)

$$(\mu_i^\alpha + z_i \psi^\alpha F)$$

$$min\left(G = \sum_\alpha^\phi \sum_i \boldsymbol{n_i^\alpha \mu_i^{el,\alpha}}\right)$$

$$n^e = \sum_\alpha^\phi \sum_i (\boldsymbol{n_i^{e,\alpha}})$$



Phase equilibrium

$$\mu_i^{el,\alpha}(\boldsymbol{N^\alpha}) = \mu_i^{el,\beta}(\boldsymbol{N^\beta}) \Leftrightarrow f_i^\alpha(\boldsymbol{N^\alpha}) = f_i^\beta(\boldsymbol{N^\beta})$$

$$\boldsymbol{N} = \boldsymbol{N^\alpha} + \boldsymbol{N^\beta}$$

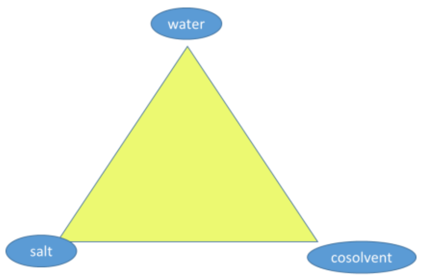
Reaction equilibrium

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

$$n^e = \sum_i \boldsymbol{n_i^e}$$

All species need to be identified with formation Gibbs energy and non-ideality model (fugacities)

CONCLUSION



- Ternary system investigated : water, cosolvent, salt

- Different properties of interest must be included in model construction
  - Solvent activity coefficients <-> salting in / salting out (VLE)
  - Ion Gibbs energy of transfer <-> species (ion) reactivity
  - Mean ionic activity coefficients <-> SLE and reactivity

- Statistical equation of state allows
  - EoS => HP/HT
  - Group contribution EoS => can be extended to complex molecules
  - Visualize microscopic effects (impact of ion pairing)

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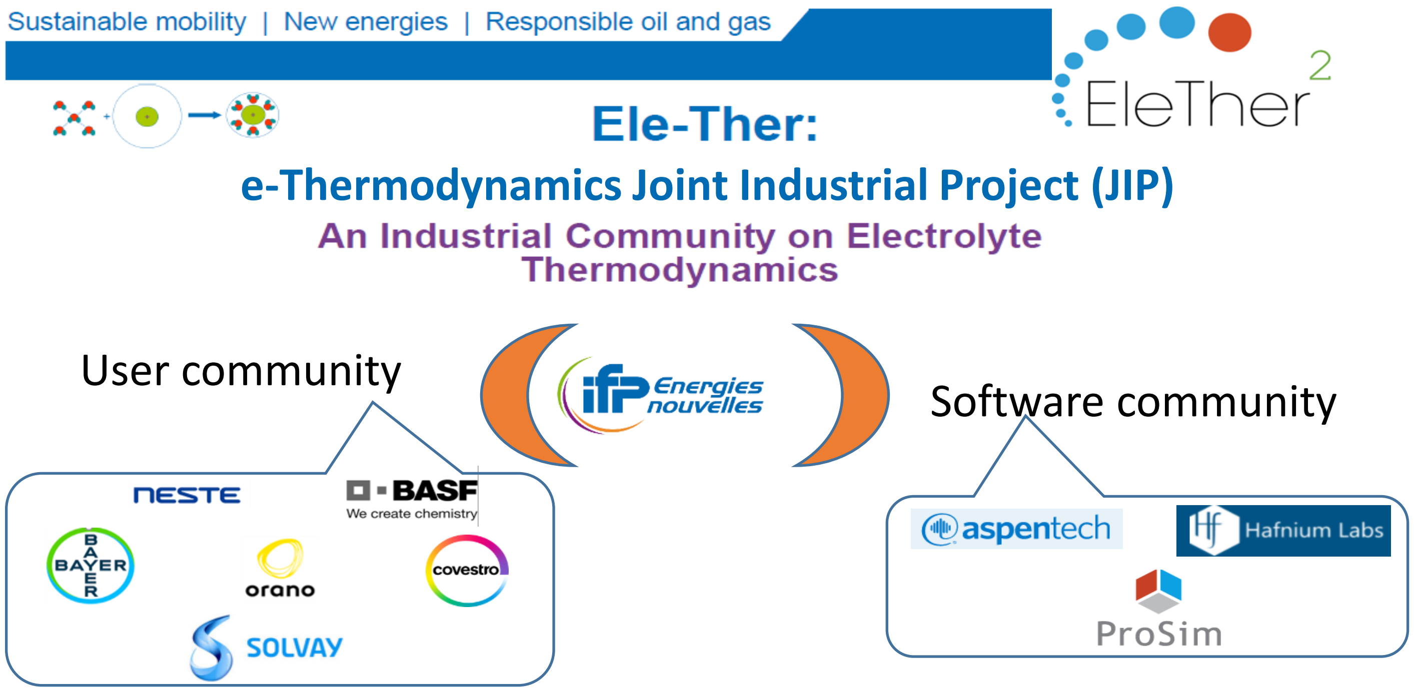

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