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

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Experimental data:
- Trends?
- Consistency?
- Uncertainty?

Trends Explained by:
- Regression
- Physical principles

Fundamental phenomena

Model = Equation of state
Construction + parameters

Reactivity = formation properties

Reactive flash algorithm

Uncertainty propagation

Process simulator
Equations of state

\[ A(T, V, N) = A^{ig} + A^{res} \]

\[ RT \ln \varphi_i = RT \ln \varphi_i \gamma_i = \frac{\partial A^{res}}{\partial N_i}_{T,V,N\neq i} - RT \ln Z \]

Gibbs energy = activity coefficient

\[ G(T, P, N) = G^{idMix} + G^E \]

\[ RT \ln \gamma_i = \frac{\partial G^E}{\partial N_i}_{T,P,N\neq i} \]

Ideal gas

Electrolyte liquid

Ideal mixture (liquid)

Electrolyte liquid

\[ A^{res} = A^{uncharg} + A^{condense} + A^{charg} + A^{electro} \]

\[ G^E = G^{ion-ion} + G^{SR} + G^{ion-solvent} \]
CONSTRUCTION OF ION-PAIRING MODEL

\[ A_{res} = A^h_c + A_{disp} + A_{assoc} + A^{MAL} + A_{polar} + A^{elec} + A^{Born} \]

- **Van der Waals forces**
- **Polar interaction**
- **Solvent-solvent + solvent-ion**
- **Repulsion**

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

Hydrometallurgical Processes:

System:

Properties / phases:

VLE
speciation
SLE
LLE

Fig. 3. Flow sheet of the process described in the Italian patent No. RM2012A000374.
The activity coefficients are an indication of non-idealities

\[
\gamma_i P = x_i P^\sigma_i \gamma_i
\]

\[
RT \ln \gamma_i = \sum \left( \frac{\partial A_{res}^{\text{res}}}{\partial N_i} \bigg|_{T,V,N_{j\neq i}} - \frac{\partial A_{res}^{\text{res}}}{\partial N_i} \bigg|_{T,V,N_{j\neq i}}^{\text{ref}} \right) - RT \ln \frac{\nu}{\nu^{\text{ref}}}
\]
DATA ANALYSIS

\[ \gamma_i = \frac{y_i \times P}{x_i \times p_i^\sigma} \]

**Water/Methanol/Potassium acetate**

- Salting-out
- Without Salt
- 2.06M KAc
- 4.16M KAc
- 6.23M KAc

Almost no impact!

**Water activity coefficient**

- Salting-in ==> increasing with salt concentration

**Methanol activity coefficient**

- Methanol composition (salt-free) in liquid phase (mol/mol)
- Water/Methanol/Potassium acetate

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CONTRIBUTION TO THE SALTING-IN/SALTING-OUT EFFECT

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

\[ i = \text{solvent} \]

\[ 298.15K \]
Gibbs energy of transfer:

\[ RT \ln (\gamma_i^{s,0}) = \mu_i^{s,0} - \mu_i^0 \]

\( i = \text{ion} \)

Activity coefficient of the solutes at infinite dilution in the solvent

Reaction equilibrium

\[ \prod_i (x_i y_i)^{\nu_i} = \prod_i \left( \frac{f_i}{f_i^{\text{ref}}} \right)^{\nu_i} = \exp \left( -\frac{\sum_i \nu_i \mu_i^{\text{ref}}}{RT} \right) = K \]

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

\[ = \prod_i \left( \frac{f_i^{s,0}}{f_i^0} \right)^{\nu_i} = \prod_i (\gamma_i^{s,s})^{\nu_i} \]
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)

\[ \ln (\gamma_i^{*S}) = \sum \left( \left. \frac{\partial A_{res}^T}{\partial N_i} \right|_{T,V,N_j \neq i}^{x=0,S} - \left. \frac{\partial A_{res}^T}{\partial N_i} \right|_{T,V,N_j \neq i}^{x=0,w} \right) - RT \ln \left( \frac{v_x^{x=0,S}}{v_x^{x=0,w}} \right) \]

where \( i = \text{ion} \)

Water-methanol-NaCl at 298.15K

- ln(gamma_transfer)
- x methanol

Graph showing the relationship between ln(gamma_transfer) and x methanol with various curves labeled as hc, disp, ass, nahs, polar, msa, born, lnZ, and sum.
SLE (LIXIVIATION; PRECIPITATION)

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

\( i = \text{ion} \)

SLE

\[ (x_{B_{aq}} \gamma_{B_{aq}}^+) v_A (x_{B_{aq}} \gamma_{B_{aq}}^-) v_B = K = \exp^{\frac{\mu_{AB}}{RT}} \]

If activity coefficient is defined in mixed solvent

\[ K^s = K \prod \gamma_{*}^{s}^{v_i} \]

MIAC : from potentiometry

\[ RT \ln(\gamma_{+/−}) = \mu_i - \mu_i^{\text{id},s} \]
MIAC CONTRIBUTIONS

Water + Methanol + NaCl

Water + Ethanol + NaCl
\[ \ln(\gamma_{\pm}) = \sum \left( \frac{\partial A^\text{res}}{\partial N_i} \bigg|_{T,V,N_{j\neq i}}^{s} - \frac{\partial A^\text{res}}{\partial N_i} \bigg|_{T,V,N_{j\neq i}}^{x=0,s} \right) - RT \ln \frac{\nu^s}{\nu^{x=0,s}} \quad i = \text{ion} \]
LLE (EXTRACTION)

Phase equilibrium

\[
\mu_i^{\alpha} + z_i \psi^\alpha F' = 0
\]

\[
\begin{aligned}
\mu_i^{\text{el},\alpha}(N^\alpha) &= \mu_i^{\text{el},\beta}(N^\beta) \\
&= f_i^\alpha(N^\alpha) = f_i^\beta(N^\beta) \\
N &= N^\alpha + N^\beta
\end{aligned}
\]

Reaction equilibrium

\[
\begin{aligned}
\sum_i \phi_i \sum_{\alpha} n_i^{\alpha,\alpha} & \\
\sum_i \mu_i \nu_i &= 0 \\
\Pi_i \left( \frac{f_i}{f_i^{\text{ref}}} \right)^{\nu_i} &= \exp \left( \frac{-\sum_i \nu_i \mu_i^{\text{ref}}}{RT} \right) = K \\
n^e &= \sum_i n_i^e
\end{aligned}
\]

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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