The Refined Electrolyte-NRTL Model applied to CO$_2$-H$_2$O-alkanolamine systems

- Equilibrium model predictions
- Implementation into the CO2SIM simulator.

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Outline

• Equilibrium problem statement

• The refined electrolyte-NRTL model
  – Theory
  – Predictions of partial pressures, speciation and heat of absorption

• Implementation into CO2SIM
Equilibrium: Problem statement

Vapour – liquid equilibria (VLE):
\[ \phi_i y_i p = \gamma_i x_i E_i \psi_i \]

Chemical equilibria (liquid phase):
\[
\begin{align*}
\min & \quad G(n) \\
\text{s.t.} \quad & \quad An = b \\
& \quad K_{eq,j} = \prod_{i=1}^{g} (\gamma_j x_j)^{v_{ij}} \\
& \quad n_i \geq 0
\end{align*}
\]

Water ionization:
\[ 2H_2O = H_3O^+ + OH^- \]

Dissociation of carbon dioxide:
\[ 2H_2O + CO_2 = H_3O^+ + HCO_3^- \]

Dissociation of bicarbonate:
\[ H_2O + HCO_3^- = H_3O^+ + CO_3^{2-} \]

Dissociation of protonated amine:
\[ H_2O + R_1R_2NH_2^+ = H_3O^+ + R_1R_2NH \]

Carbamate reversion to bicarbonate:
\[ H_2O + R_1R_2NCOO^- = R_1R_2NH + HCO_3^- \]
Model structure

General model structure:

**Helmholtz energy formulation (EOS):**

\[ A = A^{SR} + A^{LR} \]

\( A = A_{\text{classical eos}} + A_{\text{DH/MSA}} + (A^{\text{Born}}) \)

**Excess Gibbs energy formulation (y):**

\[ G^E = G^{E,SR} + G^{E,LR} \]

\( G^E = G^{E,NRTL} + G^{E,DH/MSA} + (G^{E,Born}) \)

The latter structure is adopted in the e-NRTL framework.

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**SR**
**Short range interactions**

- \( G^E \): E-NRTL, UNIQUAC etc.
- EOS: cubic, CPA etc.
- Parameter estimation

**LR**
**Long range interactions**

- Coulombic interactions
- Stronger interactions
- Great deviations from ideality
- Debye-Hückel/MSA term
- Consistency issues
- Weak theoretical basis

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Model requirements (rigorous models)

1. Thermodynamic consistency
2. Must be able to deal with mixed solvents and molecular solutes
3. Reasonable computational effort
4. Reasonable number of parameters to be estimated
5. Versatility (easily applied to different systems)
6. Accurate predictions for variable loadings and process conditions
   1. Partial pressure of CO$_2$ and amine
   2. Speciation (distribution of species)
   3. Heat of absorption (important for energy consumption in stripper)
Models found in literature

Numerous models found in literature. Most are $G^E$ based.

Non-rigorous (empiric) models

- Kent-Eisenberg, (Desmukh-Mather)
- Simple structure (+)
- Few parameters (+)
- Limited usefulness (-)
  → Not speciation, $\gamma_{H2O}$, $\gamma_{amine}$ and $\Delta H_{abs}$
- May be suited for early-phase studies

EOS based models ($\varphi$ - $\varphi$)

Few models found – weaker, but growing basis.

- Fürst - Renon (Cubic EOS + MSA)
- CPA models (cubic + association)
- Versatile models (+)
- Complex models (-)
- Mixing rules (-)
- Less experience and know-how (-)
- Many parameters to be estimated (-)

$G^E$ models ($\gamma$-$\varphi$)

- E-NRTL, Pitzer, UNIFAC, UNIQUAC, etc.
- More complex (-)
- Often many parameters (-)
- Better predictability (+)
- Parameter databases (+)
- Much experience and know-how (+)
- Especially e-NRTL is much used

Most work found in literature is done in this field.
The Electrolyte-NRTL model

- Maybe the most used (rigorous) model for industrial electrolyte systems

- Simplifying assumption made in differentiation to yield the activity coefficients

- Inconsistent for multi-ionic solutions, 
  \[ G^E \neq RT \sum_{i} n_i \ln \gamma_i \]
  - Multi-ionic: Multiple cations and/or anions

- Recent paper by Bollas et al.\(^2\) presented a corrected e-NRTL model
  \[ RT \ln \gamma_i = \frac{\partial G^E}{\partial n_i} \]
  \[ \frac{n_{g}^{E,SR}}{RT} = \sum_{m} n_{m} \left( \frac{\sum_{j} C_{j} n_{j} G_{jm} \tau_{jm}}{\sum_{j} C_{j} n_{j} G_{jm}} \right) + \sum_{c} n_{c} |z_{c}| \left( \sum_{a} Y_{a} \frac{\sum_{j} C_{j} n_{j} G_{jc,ac} \tau_{jc,ac}}{\sum_{j} C_{j} n_{j} G_{jc,ac}} \right) \]
  + \sum_{a} n_{a} |z_{a}| \left( \sum_{c} Y_{c} \frac{\sum_{j} C_{j} n_{j} G_{ja,ca} \tau_{ja,ca}}{\sum_{j} C_{j} n_{j} G_{ja,ca}} \right) \]


Refined vs. unrefined e-NRTL

Refined e-NRTL:
- Almost no applications so far
- No parameters in literature
- Complex model equations
- (Complex parameter definitions)

Original e-NRTL:
- Inconsistent
- (Complex parameter definitions)

+ Less complex model equations
+ Parameters in literature
+ Implemented in Aspen Plus

\[
\frac{1}{x_{\text{in}}} \ln \gamma_e = \sum \frac{N_a}{\sum N_{\alpha'}} \left( \sum N_{\alpha} G_{\text{ref},\alpha} \gamma_{\alpha} \right) + \sum \frac{N_a}{\sum N'_{\alpha'}} \left[ G_{\text{ref},\alpha} \left( \sum \frac{N_{\alpha}}{\sum N_{\alpha'}} \left( \sum \frac{N_{\alpha}}{\sum N_{\alpha'}} \right) \right) \right] + \sum \frac{N_a}{\sum N'_{\alpha'}} \left[ G_{\text{ref},\alpha} \left( \sum \frac{N_{\alpha}}{\sum N_{\alpha'}} \right) \right]
\]

\[
= \sum \frac{N_a}{\sum N'_{\alpha'}} \left[ G_{\text{ref},\alpha} \left( \sum \frac{N_{\alpha}}{\sum N_{\alpha'}} \right) \right]
\]

\[
\frac{1}{Z_{x_{\text{in}}}} \ln \gamma_e = \sum \frac{X_e}{\sum X_{\alpha'}} \left( \sum X_{\alpha} G_{\text{ref},\alpha} \gamma_{\alpha} \right) + \sum \frac{X_e}{\sum X'_{\alpha'}} \left[ G_{\text{ref},\alpha} \left( \sum \frac{X_{\alpha}}{\sum X_{\alpha'}} \left( \sum \frac{X_{\alpha}}{\sum X_{\alpha'}} \right) \right) \right] + \sum \frac{X_e}{\sum X'_{\alpha'}} \left[ G_{\text{ref},\alpha} \left( \sum \frac{X_{\alpha}}{\sum X_{\alpha'}} \right) \right]
\]

\[
= \sum \frac{X_e}{\sum X'_{\alpha'}} \left[ G_{\text{ref},\alpha} \left( \sum \frac{X_{\alpha}}{\sum X_{\alpha'}} \right) \right]
\]
Equilibrium model development

- Stand-alone equilibrium model is developed
- Solves phase and chemical equilibrium
  - Speciation, partial pressures, heat of absorption
- Chemical equilibrium solved by using non-stoichiometric Gibbs energy minimization routine
- SRK or Peng-Robinson EOS for vapour phase.
- Pitzer-Debye-Hückel and Born term for long range forces
- Refined electrolyte-NRTL model implemented in the RGrad language
  - RGrad is a tailor made language that performs analytical differentiations \(^3\)
  - Verified through implementation in FORTRAN and comparison with Bollas et al.
- Electrolyte interaction parameters fitted to PCO\(_2\).
  - H\(_2\)O-NaCl-KCl system \(\rightarrow\) 4 interaction parameters \((\tau_{\text{salt,salt}} = 0)\)
  - H\(_2\)O-MEA-CO\(_2\) system \(\rightarrow\) 56 parameters!
  - Major drawback of the e-NRTL framework

Model predictions

Partial pressure of CO₂, 30wt% MEA

Electrolyte interaction parameters fitted to $P_{CO2}$
Molecule-Molecule interaction parameters may be retained from original e-NRTL model
Heat of absorption and speciation, 30wt% MEA

- Over-prediction
- Revise carbamate constant
- Calculated rigorously:

\[ H_{abs} = \sum_i \left( h_i^0 + h_i^E \right) \Delta n_i + h^{phys.abs} \]

\[ h_i^E = RT^2 \left( \frac{\partial \ln \gamma_i}{\partial T} \right)_{P,\infty} \]

\[ h^{phys.abs} = RT^2 \left( \frac{\partial \ln H_{CO_2}^\infty}{\partial T} - \frac{\partial \ln \varphi_{CO_2}}{\partial T} + \frac{\partial \ln \Phi_{Poynting}}{\partial T} \right)_{P,\infty} \]

- Minimization routine
- Good predictions for major species
- Problems with predicting free CO\(_2\)

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Evaluation of activity coefficients

- Activity coefficients for CO₂ calculated from N₂O solubility measurements and the N₂O analogy⁴

\[ \frac{H_{\text{CO}_2}}{H_{\text{CO}_2}^\infty} = \frac{H_{\text{N}_2\text{O}}}{H_{\text{N}_2\text{O}}^\infty}; \quad \gamma_{\text{CO}_2} = \frac{H_{\text{CO}_2}}{H_{\text{CO}_2}^\infty} \]

- When fitted to \( P_{\text{CO}_2} \), activity coefficients may not represent the reality
- Subject to further study

The CO2SIM simulator

- Developed for simulating novel solvent systems
- Possibility of building complex flowsheets for performance studies testing and design (used for studying alternative process configurations)
- Stable solver numerical methods
- Fast convergence
- Graphical user interface

- The refined e-NRTL model is implemented in CO2SIM
  → Converted to FORTRAN
- Simulations based on pilot plant runs are performed
- Only absorber is studied here
The CO2SIM simulator: GUI
Simulation results

Example: Simulations based on NTNU/SINTEF pilot runs

Aspen simulations performed using ratebased Radfrac in Aspen Plus v7.1
Simulation results

Example: Simulations based on NTNU/SINTEF pilot runs

Equilibrium model will be continuously improved in order to get better predictions
Conclusions and further work

• Refined e-NRTL implemented in both RGRAD and FORTRAN
  • Good overall predictions
  • Problem with predicting free CO₂
  • Work to be done on physical activity coefficients and parameter estimation
  • Compare with other thermodynamic models (e.g. UNIQUAC, EOS mod.)

• CO2SIM implementation
  • Refined e-NRTL is implemented in CO2SIM
  • Results demonstrate need for rigorous thermodynamic calculations
  • Pilot rig at NTNU/SINTEF is simulated.
  • Analysis will be extended to the whole pilot, not just absorber, and to other pilot results
Thank you for your attention.