Evaluation of parameter fitting procedures for rigorous equilibrium model development

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Outline

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Motivation

• Rigorous models are needed for optimized process design and operation
• The models need to cover all possible operating conditions
• Thermodynamic models contain many parameters
• Parameters have very variable sensitivity
• Fitting is time consuming
• Robust and structured methods are needed
Available Models

- e-NRTL
- e-UNIQUAC
- e-EOS
- Wilson
- Regression models
  - Kent-Eisenberg
  - Lee-Mather
  - Polynomials

- Simple to implement
- Semi-empirical
- Predicting all partial pressures
- Speciation
- Thermal properties
- Interpolation and extrapolation in temperature, concentration and loading
Choosing parameters to regress

\[ \tau_{ij} = \exp\left( -\frac{\Delta u_{ij}}{RT} \right) = \exp\left( -\frac{a_{ij}}{T} \right) \]

\[
\begin{bmatrix}
0 & a_{12} & \cdots & a_{1n} \\
a_{21} & 0 & \cdots & a_{2n} \\
\vdots & \vdots & \ddots & \vdots \\
a_{n1} & a_{n2} & \cdots & 0
\end{bmatrix} \rightarrow 2 \times \left( n \times (n-1) \right)
\]

Old

\[ a_{ij} = a_{ij}^0 + T \times a_{ij}^T \]

New

\[ a_{ij} = u_{ij} - u_{ij} \text{ and } u_{ij} = u_{ij}^0 + u_{ij}^T (T - 298.15) \]

\[
\begin{bmatrix}
u_{11}^0 & u_{12}^0 & \cdots & u_{1n}^0 \\
u_{12}^0 & u_{22}^0 & \cdots & u_{2n}^0 \\
\vdots & \vdots & \ddots & \vdots \\
u_{1n}^0 & u_{2n}^0 & \cdots & u_{nn}^0
\end{bmatrix} \rightarrow \begin{bmatrix}
u_{11}^T & u_{12}^T & \cdots & u_{1n}^T \\
u_{12}^T & u_{22}^T & \cdots & u_{2n}^T \\
\vdots & \vdots & \ddots & \vdots \\
u_{1n}^T & u_{2n}^T & \cdots & u_{nn}^T
\end{bmatrix} \rightarrow 2 \times \left( \frac{n \times (n+1)}{2} \right)
\]
Choosing parameters to regress, Cont.

- **Molecules**
  - Phase equilibrium data
  - Thermal properties

- **Ions**
  - Neglecting pairs using sensitivity analysis
    - Very time consuming
    - Not universal
    - System specific
  - Neglecting pairs with less effect
    - System specific
  - Neglecting pairs regarding their charges, big number for ions with the same charge
Comparison of Different Experimental Data Sets at 120°C & 30 Wt%
Overall approach

• Preferably not to use gradient based and initial guess sensitive method in early steps.
  – Pattern search
  – Simplex
  – SQP or Line-search

• All methods are bounded
  – Accuracy in extrapolation to higher or lower temperatures

• Neglecting temperature sensitivity in first round and add them in 2\textsuperscript{nd} round, or considering both in the same time
Pattern-Search method

• Meaning
  – Directly without any derivative
  – Search in different directions

• Procedure
  – Start from "initial point" and evaluate the function based on pattern
  – Increase the mesh size and repeat the evaluation if a lower function value has been found, otherwise decrease the mesh size and repeat the procedure
Pattern-Search method, Cont.

- Definitions
  - Pattern: A set of vectors that indicates search direction: \( v_1=[1 \ 0], v_2=[0 \ 1], v_3=[-1 \ 0], v_4=[0 \ -1] \);
  - Mesh: A set of points that will be evaluated to find the best point among them
  - Mesh Size: Multiplier for the direction vectors to generate new mesh points
  - Polling: Evaluation of function values at new mesh point
Pattern-Search method, Cont.

Flow chart of a search
Objective function selection

- **method1**: \( |f_{\text{exp}} - f_{\text{calc}}| \)
- **method2**: \( \text{dev} = \frac{(f_{\text{exp}} - f_{\text{calc}})}{f_{\text{exp}}} \)
- **method3**: \( \text{dev} = \frac{(f_{\text{exp}} - f_{\text{calc}})}{f_{\text{calc}}} \)
Lack of experimental data

High Temperatures

$P_{CO_2}$ for AMP system in 100°C and 30 wt% of AMP

$P_{CO_2}$ for AMP system in 120.15°C
Lack of experimental data

Continuity of results

$P_{\text{CO}_2}$ for AMP system in 100°C and 30 wt% of AMP

80 points

Lack of experimental data
Lack of experimental data

Other partial pressures
Lack of experimental data

High loadings

Partial pressure of MEA, 30 wt% MEA, 333.15K
Conclusions

• UNIQUAC model has a very good potential to describe electrolyte systems, beside its simplicity
• The approach for disregarding interaction parameters shows good performance
• Pattern-search method can handle optimization of parameters in these systems easily and efficiently
• Use of available experimental data, without any additional judgment, will not lead to a good model
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