Evaluation of parameter fitting procedures for rigorous equilibrium model development

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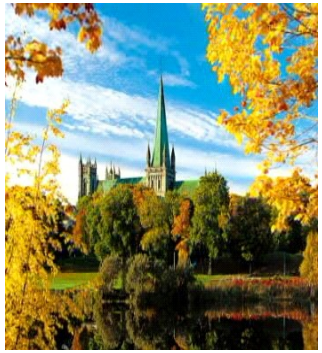


Outline

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- Available Methods
- Choosing parameters to regress
- Raw data selection
- Overall approach
- Pattern-Search method
- Objective function selection
- Lack of experimental data
- Conclusions

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

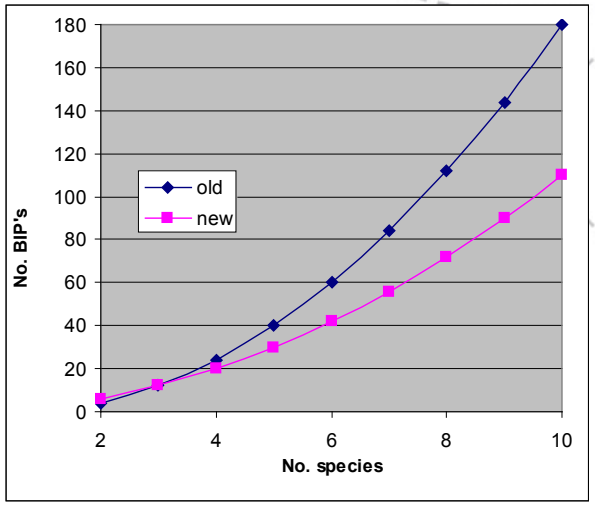
$$\tau_{ij} = \exp\left(-\frac{\Delta u_{ij}}{RT}\right) \equiv \exp\left(-\frac{a_{ij}}{T}\right)$$

Old

$$a_{ij} = a_{ij}^{0} + T \times \grave{a}_{ij}^{T}$$

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

New $\quad a_{ij} = u_{ij} - u_{jj}$ and $u_{ij} = u_{ij}^{0} + u_{ij}^{T}\left(T - 298.15\right)$



$$u^{0} = \begin{bmatrix} u_{11}^{0} & u_{12}^{0} & \cdots & u_{1n}^{0} \\ u_{12}^{0} & u_{22}^{0} & \cdots & u_{2n}^{0} \\ \vdots & \vdots & \ddots & \vdots \\ u_{1n}^{0} & u_{2n}^{0} & \cdots & u_{nn}^{0} \end{bmatrix} \quad u^{T} = \begin{bmatrix} u_{11}^{T} & u_{12}^{T} & \cdots & u_{1n}^{T} \\ u_{12}^{T} & u_{22}^{T} & \cdots & u_{2n}^{T} \\ \vdots & \vdots & \ddots & \vdots \\ u_{1n}^{T} & u_{2n}^{T} & \cdots & u_{nn}^{T} \end{bmatrix} \longrightarrow 2 \times \left(\frac{n \times \left(n+1\right)}{2}\right)$$

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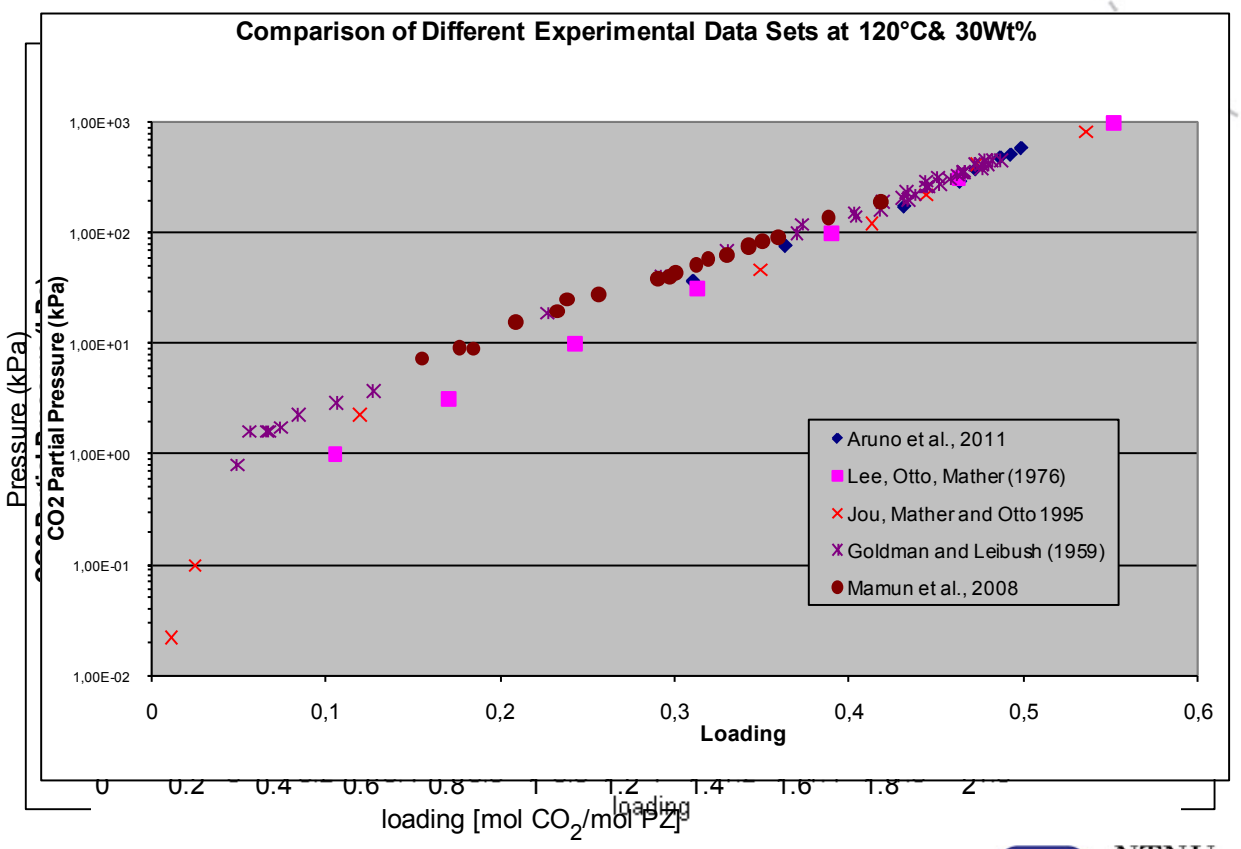
Choosing parameters to regress, Cont.

- 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

Raw data selection



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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 2nd round, or considering both in the same time

Pattern-Search method

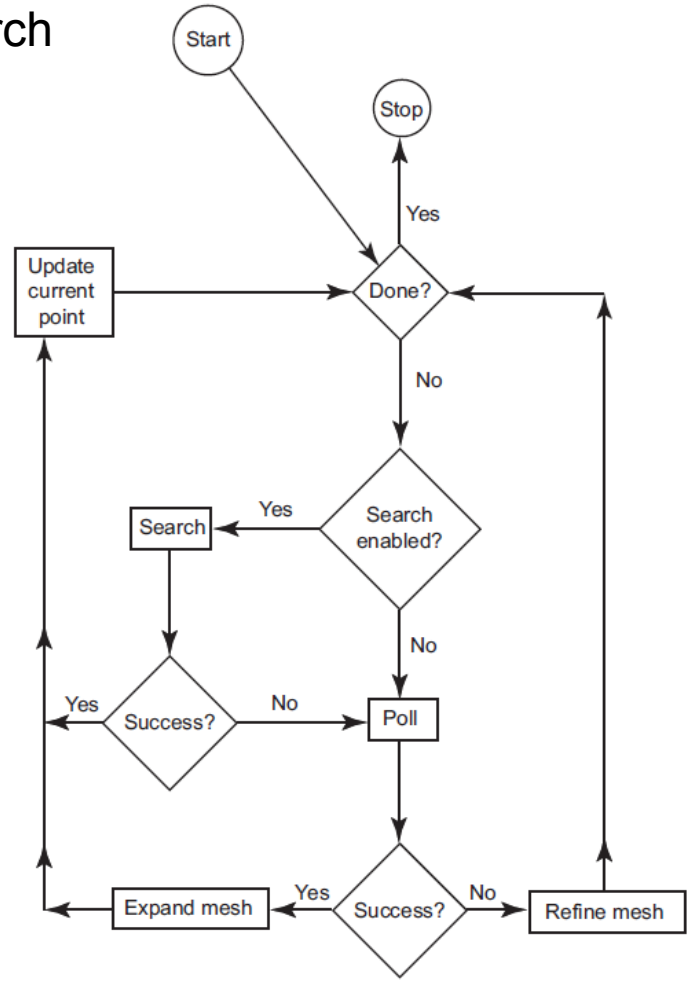
- Meaning
  - Directly without any derivative
  - Search in different directions
- Procedure
  - Start from ”initial point” and evaluate the function based on pattern
  - Increase the mesh size and repeat the evaluation if a lower function value has been found, otherwise decrease the mesh size and repeat the procedure

Pattern-Search method,Cont.

- Definitions
  - Pattern: A set of vectors that indicates search direction: v1=[1 0], v2=[0 1],v3=[-1 0];v4=[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



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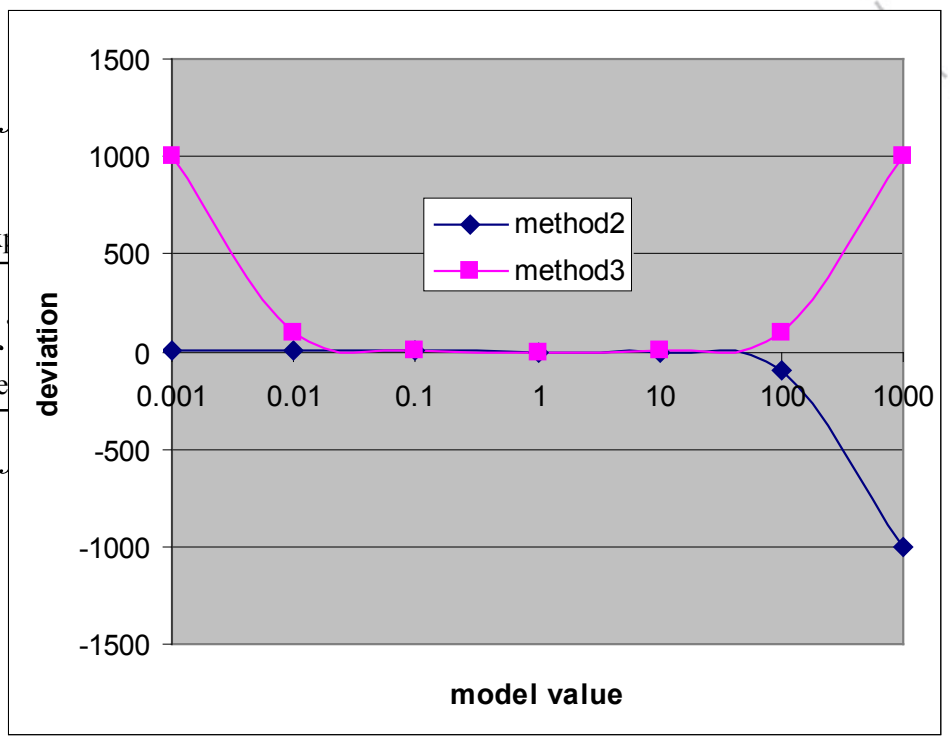
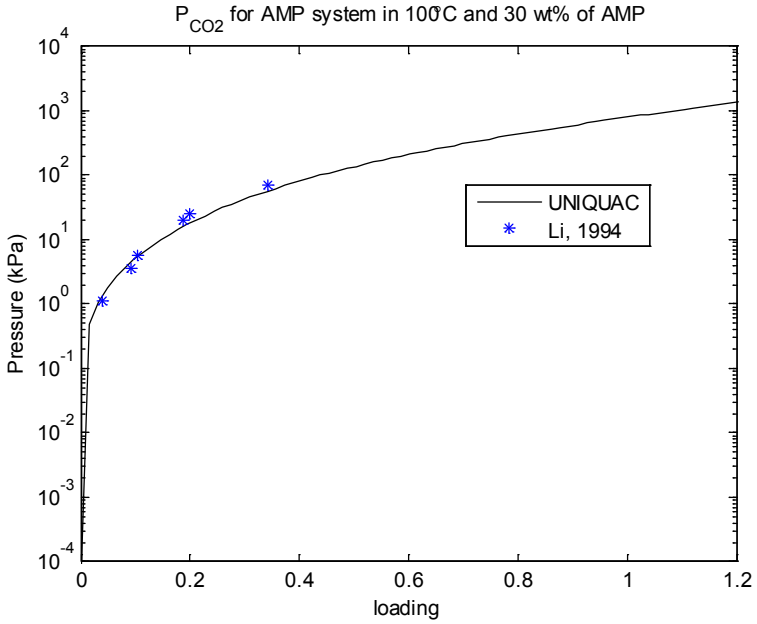
Objective function selection

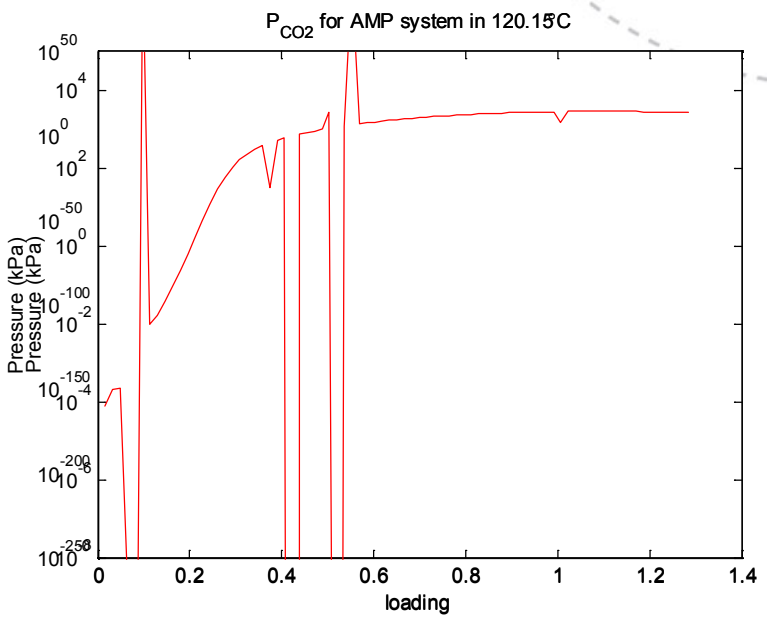
- $method1: \left| f_{\exp} - \right.$
- $method2: dev = \frac{\left(f_{\exp} \right.}{}$
- $method3: dev = \frac{\left(f_{e} \right.}{}$



Lack of experimental data

High Temperatures





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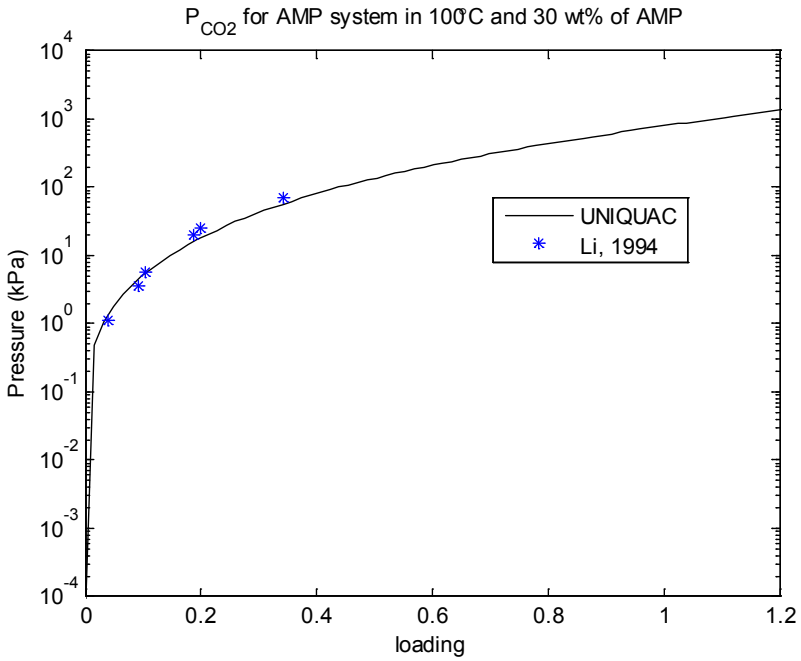
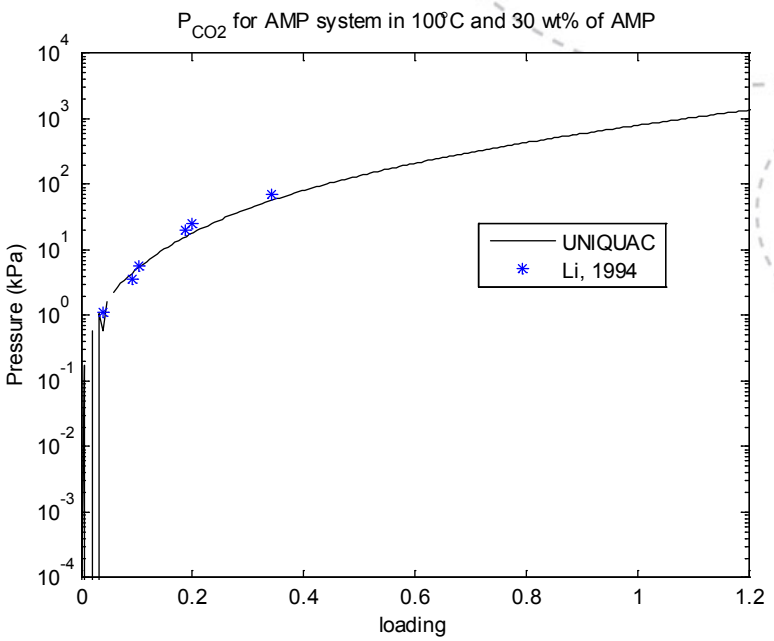
Lack of experimental data

Continuity of results



80 points



200 points

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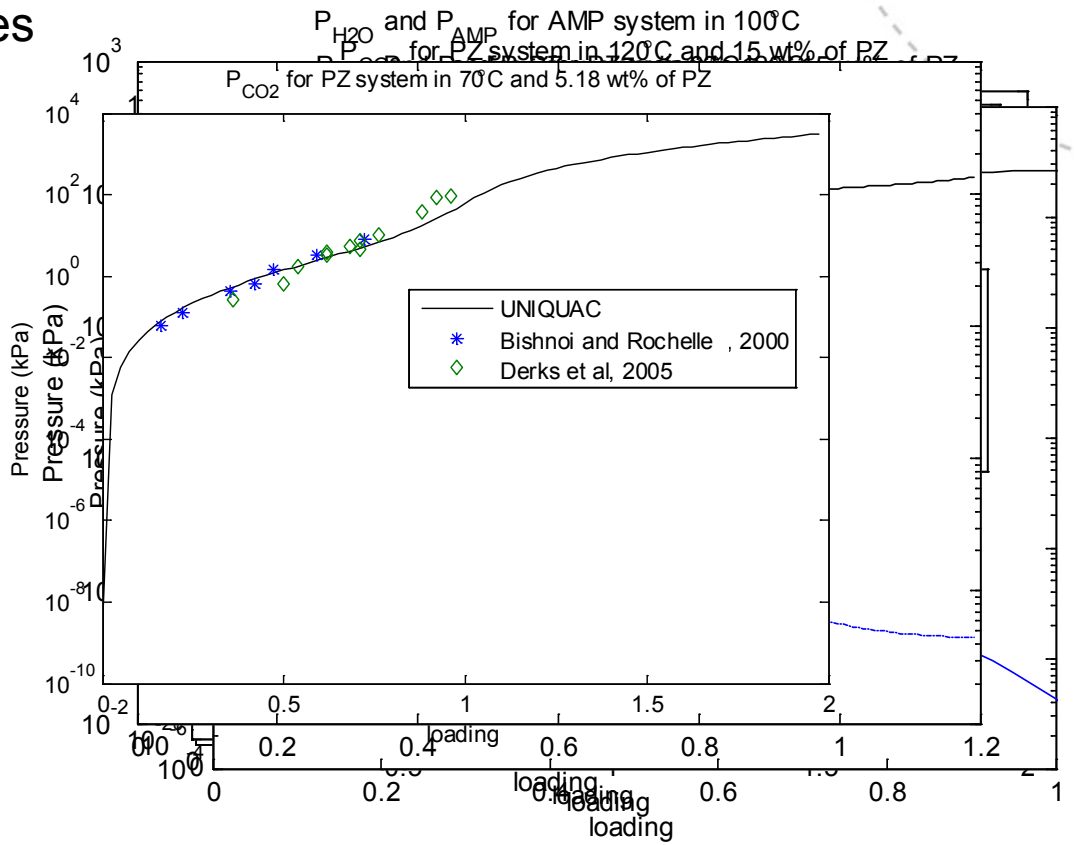
Lack of experimental data

Other partial pressures



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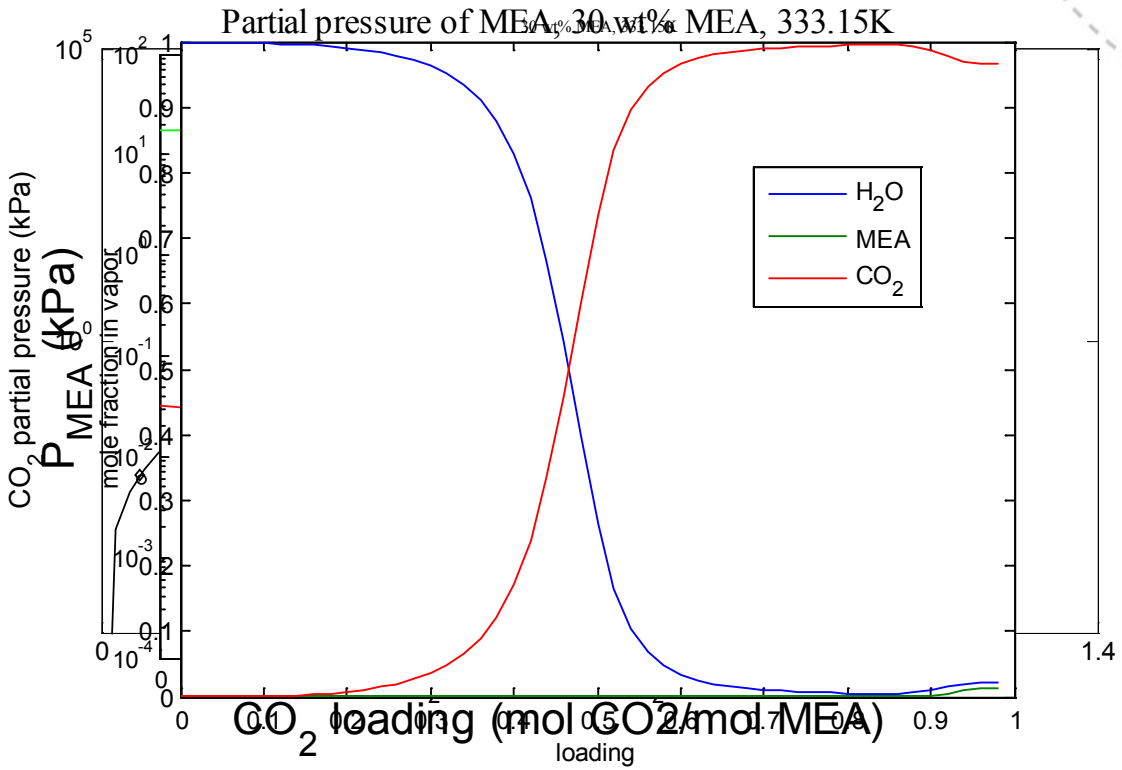
Lack of experimental data

High loadings



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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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Thanks for your attention

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