Thermodynamics modeling of the HIX part of the Iodine – Sulfur thermocycle

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Iodine – sulfur thermocycle for hydrogen production

\[
\begin{align*}
\text{SO}_2 + \text{H}_2\text{O} + \frac{1}{2} \text{O}_2 & \xrightarrow{[850 \, ^\circ\text{C}]} \text{H}_2\text{SO}_4 \\
\text{I}_2 + \text{SO}_2 + 2 \text{H}_2\text{O} & \rightarrow \text{H}_2\text{SO}_4 + 2 \text{HI} & [120 \, ^\circ\text{C}]
\end{align*}
\]

P. Carles / Thermodynamic modeling of HIx part of the Iodine – Sulfur thermocycle
Thermodynamics challenges of HIX system

“...The sulfuric acid decomposition section of this process can be simulated accurately, but other sections (acid generation and hydrogen iodide decomposition) illustrate the difficulty of modeling phase behavior, particularly liquid-phase immiscibility, in complex electrolyte systems.”

(Mathias 2005, Fluid Phase Equilibria)

\[ \text{HIX} = \text{HI}/\text{H}_2\text{O}/\text{I}_2 \] (nominal : HI / 5 H\text{2}O / 4 I\text{2})

- Multiphase behavior (vapor – liquid – liquid – solid),
- H\text{2}O – I\text{2} : highly immiscible liquid – liquid equilibrium system,
- HI – I\text{2} : solid – liquid equilibrium system,
- H\text{2}O – HI
  - Maximum boiling / low pressure azeotrope,
  - Strong electrolytic system,
  - Liquid – liquid equilibrium,
- The ternary mixture has two separate liquid – liquid regions,
- Solvation reactions occur as well as poly-iodides formation in the solution.
Outline

- Iodine-Sulfure thermochemical cycle for hydrogen production
- HIx modeling Challenges
- Proposed model and identification methodology
- Validation vs experimental literature data
- Conclusions and perspectives
HIX modeling

New models:
- UNIQUAC Solvation (UQSolv)

Literature models:
- Neumann: Engels + NRTL
- Mathias et al.: electrolyte

Homogeneous model $\phi-\phi$

Equation of State

Mixture rules

PR Boston Mathias

γ Model
Symmetric convention

Equation of State

Mixture rules

γ Model
Asymmetric convention

γ Model
Symmetric convention

Ideal gas

Electrolytes

NRTL + Pitzer

Non-Electrolytes

Wilson

NRTL Neumann

Non-Electrolytes

Electrolytes

Engels Solvation

UNIQUAC

Engels Solvation

vapor Phase

liquid Phase

Heterogeneous model $\gamma-\phi$
Advantages of the model

- \(\phi-\phi\) approach:
  - No extrapolation of the vapor pressure law above critical points
  - Correct handling of mixture phase behavior above HI critical point (\(T_c=423K\))

- Equation of state: Peng Robinson w/ Boston Mathias \(\alpha\) function
  - Accurate behavior of pure components above critical points

- Mixing rule: MHV2 including non ideal liquid phase behavior via a \(G^{ex}\) model

- Activity coefficient model: Engels solvation
  - Electrolytic model but with symmetric convention so as to span the whole composition range
  - Introduces solvation complexes with several solvents

- Activity coefficient model: UNIQUAC vs NRTL:
  - Combinatorial term handles steric effect
  - Residual term accounts for non ideal liquid phase behavior (as NRTL)
Model parameter identification procedure

✓ Three binary mixtures

- $\text{H}_2\text{O} – \text{I}_2$: only UNIQUAC binary interaction parameters
- $\text{HI} – \text{I}_2$: only UNIQUAC binary interaction parameters
- $\text{H}_2\text{O} – \text{HI}$:
  - HI solvation by $\text{H}_2\text{O} \rightarrow$ equilibrium constant and solvation number
    \[
    m \text{H}_2\text{O} + \text{HI} \leftrightarrow 2\text{C}
    \]
  - UNIQUAC binary interaction parameters for $\text{H}_2\text{O}$, $\text{HI}$ and the solvation complex $\text{C}$

✓ Ternary mixture

- $\text{H}_2\text{O} – \text{HI} – \text{I}_2$: refined parameter values
## Available experimental data

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<tr>
<th>Data</th>
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<th>Data sources</th>
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<td><strong>H₂O – HI</strong></td>
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H₂O – I₂ identification results

Model prediction of iodine solubility in aqueous solution
HI – I₂ identification results

- 

Iodine melting point

Neumann Model

(exp (O'Keefe et Norman, 1982)
Ideal UNIQUAC
Neumann
UQSolv)

Solubility of Solid I₂ in HI-I₂ Solutions

- exp (O’Keefe and Norman, 1982)
- Calculated - NRTL
- Calculated - Ideal

Temperature (°C)

Mass composition of iodine (%)

0 20 40 60 80 100

0 20 40 60 80 100
Good agreement up to the azeotrope
Model prediction of LVE curve at atmospheric pressure
Ternary system $\text{H}_2\text{O} - \text{HI} - \text{I}_2$

Engels experimental data
$(0.017 < x_{\text{HI}} < 0.159)$

Liquid – liquid equilibrium data
(Norman, 1984)
H₂O – HI – I₂ identification results 1/2

Keeping identified parameters for:

- Liquid – liquid equilibrium (H₂O – I₂)
- Solid – liquid equilibrium (HI – I₂)
- Vapor – liquid equilibrium (H₂O – HI) with solvation (m H₂O + HI ⇋ 2C)

\[
\text{Criterion} = \sum_{Np} \left( \frac{P_{\text{exp}} - P_{\text{cal}}}{P_{\text{exp}}} \right)^2
\]

<table>
<thead>
<tr>
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<th>Average error (%)</th>
<th>Max error (%)</th>
<th>criterion</th>
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<tr>
<td>Neumann</td>
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<td>UQSolv</td>
<td>8.18</td>
<td>44.83</td>
<td>3.73</td>
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H$_2$O – HI – I$_2$ identification results  2/2
Conclusion and perspectives

✓ HIX non ideal and electrolytic system is modeled by an equation of state (EOS) approach with complex mixing rules including $G^E$ models.

✓ The EOS approach is well suited with expected process T and P conditions that may be higher than the HI critical point.

✓ The liquid phase non ideal behavior is modelled combining Engels solvation equations suitable for any electrolyte composition and activity coefficient UNIQUAC equation.

✓ The resulting UQsolv model predict accurately most of the experimental data available and accurate, incl. LLE, LSE and LLVE for each binary and ternary system.

✓ Largest discrepancy is found for high HI concentration mixtures where experimental data is lacking or is uncertain.

✓ Improvements are under investigation:
  
  ▪ Polyiodide ion formation
  
  ▪ HI decomposition in I$_2$ and H$_2$ for the vapor phase rich in HI