Methane Hydrate Formation Behavior in the Presence of Selected Amino Acids

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Methane Hydrate Formation Behavior in the Presence of Selected Amino Acids

Jyoti Shanker Pandey*, Yousef Jouljamal Daas, and Nicolas von von Solms

Center for Energy Resource Engineering (CERE), Department of Chemical Engineering, Technical University of Denmark,

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Introduction

What are Gas Hydrate?

- Ice-like, crystalline structures
- Common hydrate formers: methane, ethane, propane, carbon dioxide, hydrogen sulfide, nitrogen, hydrogen

```
\[ \text{water} + \text{gas} + \text{High P} + \text{Low T} \]
```

Gas storage capacity in hydrates

```
1 \text{ m}^3 \text{ Hydrate} \rightarrow \sim 164 \text{ m}^3 \text{ Gas at STP} + 0.9 \text{ m}^3 \text{ Water}
```

Water cages
Application of Gas Hydrate

Natural Gas Hydrate
- Permafrost onshore
  - Methane Production
- Marine Sediments
  - Methane Production

Man Made Hydrate
- Gas Capture & Separation
  - CO₂/CH₄ Separation
- Desalination
  - CO₂ hydrate based
- Refrigeration
  - CO₂ hydrate based

Flow Assurance in Oil & gas

Methane Hydrate Formation Behavior in the Presence of Selected Amino Acids
Chemicals For Gas Hydrates

Chemicals for Gas Hydrate

- Accelerate hydrate formation
  - Thermodynamic Acceleration
  - Kinetic acceleration

- Delay hydrate formation
  - Thermodynamic delay
  - Kinetic Delay

Promoters

Amino Acids?

Inhibitors
Why Amino Acids?

Available Chemicals
- Toxic
- By product of petroleum
- Create foam
- Expensive
- Large Quantity

Amino Acids
- Environment Friendly
- Non Toxic, Biodegradable
- Non Expensive
- Large Quantity
- Expensive
Objective

• Understand the kinetics of methane hydrate formation
  – In presence of Amino Acids

• Understand the role of Amino Acids
  – Promoter or Inhibitor

• Explain the mechanism
### Selected Amino Acid in this study

<table>
<thead>
<tr>
<th>#</th>
<th>Name</th>
<th>Side Chain polarity</th>
<th>Side Chain</th>
<th>Hydrophobicity/ Hydropathy Index (Kyte and Doolittle, 1982)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>L-valine</td>
<td>Non polar</td>
<td>-CH(CH₃)₂</td>
<td>4.2</td>
</tr>
<tr>
<td>2.1</td>
<td>L-methionine</td>
<td>Non polar</td>
<td>CH₃-S-(CH₂)₂</td>
<td>1.9</td>
</tr>
<tr>
<td>3.1</td>
<td>L-histidine</td>
<td>Basic polar, aromatic side chain</td>
<td>-CH₂C₃H₃N₂</td>
<td>-3.2</td>
</tr>
<tr>
<td>4.1</td>
<td>L-arginine</td>
<td>Basic polar aliphatic side chain</td>
<td>HN=C(NH₂)-NH(-CH₂)₃</td>
<td>-4.5</td>
</tr>
</tbody>
</table>
Experimental Setup

Rocking Cell (PSL Germany)

- Rocking Rate, Rocking Angle
- Volume
- Temperature Ramping, Constant Temperature

- A- Bathtub
- B- High Pressure Cell
- C- Rocking Balls
Temperature Scheme

Isothermal Experiment
(Fresh & Memory)

Induction Time ($t_0$)  Gas Uptake

$$uptake = \frac{\Delta n^\text{methane gas}_H}{n_{S\text{ol}}$$
Methodology

P-T Curve at Constant Volume in Batch system

Gas consumption (Gas uptake) curve
Induction time (in mins) for given Amino acids at 1 °C

- **Hydrophobic Amino Acid**
  - L-arginine
  - L-histidine
  - L-methionine
  - Reference Line L-valine

- **Hydrophilic Amino Acid**
  - L-valine

100 bar Fresh vs 70 bar Fresh

Methane Hydrate Formation Behavior in the Presence of Selected Amino Acids
Normalized Gas Uptake (m-mol/m-mmol) for given Amino acids at 1 °C

<table>
<thead>
<tr>
<th>Hydrophobic Amino Acid</th>
<th>Reference Line L-arginine</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-arginine</td>
<td>0.020</td>
</tr>
<tr>
<td>L-histidine</td>
<td>0.017</td>
</tr>
<tr>
<td>L-methionine</td>
<td>0.121</td>
</tr>
<tr>
<td>L-valine</td>
<td>0.123</td>
</tr>
</tbody>
</table>

Hydrophilic Amino Acid

Hydrophobic Amino Acid

Methane Hydrate Formation Behavior in the Presence of Selected Amino Acids
Summary

• Hydrophobic amino acids, as promoter while hydrophilic amino acid as inhibitor

• Hydrophobic amino acids in gas hydrate promotion such as gas storage, capture etc

• Hydrophilic amino acids in flow assurance in Oil & Gas pipeline

• Amino acid shows memory effect in Induction time, kills memory effect in gas uptake.

• Increase in pressure create higher driving force, thus lower induction time and higher gas uptake

• L-methionine is best promoter while L histidine is best inhibitor.
Mechanism

Water molecules in liquid phase are connected through a hydrogen bond network (a) In the system without inhibitor, liquid water molecules close to the hydrate surfaces (e.g. nuclei and bulk surfaces) or solid substrates (e.g. reactor walls, foreign impurities) participate in hydrate formation. (b) The adsorption inhibition hypothesis involves adsorption of the inhibitors on the hydrate surface or any nucleating sites, inhibiting hydrate formation. (c) The perturbation inhibition hypothesis involves perturbation of the organization of local water molecules, preventing hydrate formation.

Less hydrophobic amino acids disrupt hydrogen bonds between water molecules to inhibit hydrate formation while more hydrophobic amino acids strengthen the local organization of the water structure. That
AT CERE

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- Transport Processes and Properties
- Mathematical modeling
- Material science
- Petroleum Technology
- Enhanced Oil Recovery
- CO2 capture and gas hydrates
- Energy resources
- Biorefinery Conversions

Professor Georgios Kontogeorgis
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Gas Hydrate Research