Methane Hydrate Formation Behavior in the Presence of Selected Amino Acids

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Publication date:
2019

Document Version
Peer reviewed version

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Citation (APA):
Methane Hydrate Formation Behavior in the Presence of Selected Amino Acids

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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

![Water + Gas + High P, Low T](image)

$5^{12}, 5^{12}6^2, 5^{12}6^8$

Water cages

Gas storage capacity in hydrates

1 m$^3$ Hydrate $\rightarrow$ ~164 m$^3$ Gas at STP $+ 0.9$ m$^3$ Water

Burning hydrate
Application of Gas Hydrate

Natural Gas Hydrate
- Permafrost onshore
- Marine Sediments
  - Methane Production
  - Methane Production
- Gas Storage
  - Natural Gas Storage/Transport
- Gas Capture & Separation
  - CO₂/CH₄ Separation
- Desalination
  - CO₂ hydrate based
- Refrigeration
  - CO₂ hydrate based

Man Made Hydrate
- Flow Assurance in Oil & gas

Methane Hydrate Formation

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

- 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, Bio degradable
- Non Expensive
- Non 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 Rate, Rocking Angle
- Volume
- Temperature Ramping, Constant Temperature

**Rocking Cell (PSL Germany)**

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

Isothermal Experiment
(Fresh & Memory)

Induction Time ($t_o$)

Gas Uptake

\[ \text{uptake} = \frac{\Delta n_H^{\text{methane gas}}}{n_{\text{Sol}}} \]
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

Hydrophilic Amino Acid
Normalized Gas Uptake (m-mol/m-mmol) for given Amino acids at 1 º C

<table>
<thead>
<tr>
<th>Amino Acid</th>
<th>70 bar fresh</th>
<th>100 bar Fresh</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-arginine</td>
<td>0.020</td>
<td>0.062</td>
</tr>
<tr>
<td>L-histidine</td>
<td>0.017</td>
<td>0.015</td>
</tr>
<tr>
<td>L-methionine</td>
<td>0.021</td>
<td>0.031</td>
</tr>
<tr>
<td>L-valine</td>
<td>0.019</td>
<td>0.019</td>
</tr>
</tbody>
</table>

Hydrophilic Amino Acid

Hydrophobic Amino Acid
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.
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.
AT CERE

- Applied Thermodynamics
- 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