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

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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

Gas storage capacity in hydrates

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

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

water cages

Burning hydrate
Application of Gas Hydrate

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

- Man Made Hydrate
  - Flow Assurance in Oil & gas
    - Methane Hydrate Formation
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 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

$$uptake = \frac{\Delta n_H^{\text{methane gas}}}{n_{\text{Sol}}}$$
Methodology

P-T Curve at Constant Volume in Batch system

Gas consumption (Gas uptake) curve

Methane Hydrate Formation Behavior in the Presence of Selected Amino Acids
Induction time (in mins) for given Amino acids at 1 °C

<table>
<thead>
<tr>
<th>Amino Acid</th>
<th>100 bar Fresh</th>
<th>70 bar Fresh</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-arginine</td>
<td></td>
<td></td>
</tr>
<tr>
<td>L-histidine</td>
<td></td>
<td></td>
</tr>
<tr>
<td>L-methionine</td>
<td></td>
<td></td>
</tr>
<tr>
<td>L-valine</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Hydrophilic Amino Acid

Hydrophobic Amino Acid

Reference Line L-valine
Normalized Gas Uptake ($m$-mol/$m$-mmol) for given Amino acids at $1 \degree C$

<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>0.033</td>
</tr>
<tr>
<td>L-methionine</td>
<td>0.015</td>
<td>0.021</td>
</tr>
<tr>
<td>L-valine</td>
<td>0.019</td>
<td>0.021</td>
</tr>
</tbody>
</table>

Reference Line: L-arginine

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.
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

- 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
Group Leader

Ass Professor Nicolas von Solms
Gas Hydrate Research
Thank You

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