Hydrate Phase Equilibria of Natural Gas Mixtures Plus CO₂ in the Presence of Thermodynamic Inhibitors

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About 40% of natural gas fields are sour, producing these reservoirs involves also low temperatures combined with high pressures working conditions, presence of water and transport times, leading to the possibility of gas hydrate formations in pipelines.

Sour gas fields (The Oil and Gas Year)

Hydrate dissociation points were measured for two systems natural gas + CO₂. These measurements were conducted in the presence of 25%wt and 50%wt of thermodynamic inhibitors (methanol, ethanol and ethylene glycol or MEG).

Thermodynamic Modelling

To predict hydrate phase equilibria, the following models are used:

- **Hydrate Phase**: Van der Waals and Plateau model (1959) as implemented by Parrish and Prausnitz (1979)
- **Fluid phase**:
  - SRK-CPA (Kontogeorgis et al., 1994) with adjusted binary interaction parameters (used for systems with MEG)
  - GC-PR-CPA (Hajiw et al., 2014): The PR-CPA equation of state is coupled with a group contribution method (modified PPR78 EoS), which calculates (in a predictive way) binary interaction parameters.

**Device for hydrate dissociation point measurements**

A mixed autoclave rig has been used for hydrate dissociation point measurements. The cell volume is about 500 mL and can operate up to 400 bar and between -35°C and 50°C.

**Schematic illustration of the autoclave cell used for hydrate equilibrium studies**

Composition of the natural gas

<table>
<thead>
<tr>
<th>Compounds</th>
<th>%wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>7.00</td>
</tr>
<tr>
<td>Methane</td>
<td>84.13</td>
</tr>
<tr>
<td>Ethane</td>
<td>4.68</td>
</tr>
<tr>
<td>Propane</td>
<td>2.33</td>
</tr>
<tr>
<td>n-Butane</td>
<td>0.93</td>
</tr>
<tr>
<td>n-Propane</td>
<td>0.93</td>
</tr>
</tbody>
</table>

**Effect of the presence of carbon dioxide on the hydrate dissociation curve**

The presence of CO₂ slightly shifts the hydrate stability curve of the natural gas systems to lower temperatures (about 1°C for 10% of CO₂).

**Comparison of the hydrate dissociation curves in the presence of 25 %wt of thermodynamic inhibitors**

The system presented is the natural gas with 10% of CO₂. While ethanol and (MEG) have a similar effect, i.e. a decrease of 8°C for a same pressure, methanol is the most performant inhibitor in this case, with a shift of 13°C. The GC-PR-CPA model predicts accurately the hydrate dissociation curve for the system in pure water and with 25%wt of methanol. There a slight discrepancies for systems with ethanol. Glycols have not been added to the model yet.

- **10°C for ethanol and MEG**
- **17°C for methanol**

**Modification for associating compounds (water, methanol and ethanol)**

Data acquisition

Pressure vessel

+ coolant jacket

Stirring device

Bath and T regulator

Comparison of the hydrate dissociation curves in the presence of 25 %wt and 50 %wt of thermodynamic inhibitors

The system presented is the natural gas with 10% of CO₂. Double the quantity of thermodynamic inhibitors decreases the temperature of hydrate formation of about:

- **10°C for ethanol and MEG**
- **17°C for methanol**