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Wise, Michael; Chapoy, Antonin; Burgass, Rhoderick William; Tohidi Kalorazi, Bahman

Publication date:
2017

Document Version
Other version

Link to publication in Heriot-Watt University Research Portal

Citation for published version (APA):
Gas Hydrate and PVT Phase Equilibria
Group, Institute of Petroleum Engineering

Phase Behavior of Methane in Methanol, Ethanol and Aqueous Solutions

Michael Wise, Antonin Chapoy, Rod Burgass, Bahman Tohidi

Introduction
One of the main flow assurance challenges that faces the petroleum industry is hydrate formation, thus it is essential to understand and model the distribution of hydrate inhibitors for the design of efficient and economical gas transportation and processing operations. Thermodynamic inhibitors such as methanol, ethanol and mono-ethylene glycol (MEG) are commonly used to prevent hydrate formation, however their use entail significant Capital Expenditure (CAPEX) and Operating Expenditure (OPEX). Thus, it is essential to minimize the use of inhibitors through reliable phase behavior calculations.

Why CH₄ Solubility Measurement and Modelling
Solubility data for methane (CH₄) in methanol, ethanol and their solutions are extremely limited. The aim of this study was to measure and develop:
- Validate the experimental method using CH₄ in methanol measurements
- CH₄ in methanol and solution measurement
- CH₄ in ethanol and solutions measurements.
- BIPs CPA-SRK72 EoS
- Evaluate ternary and quaternary system predictions.

These results will assist the energy and simulation software companies as well as researchers to optimise and develop Equations of State (EoS), which will in turn increase simulation and engineering design efficiency.

Modelling
The CPA-SRK72 EoS developed by Kontogeorgis et al was used and optimized throughout this work.

\[ P = \frac{RT}{V_m - b} - \frac{a(T)}{2V_m(V_m + b)} \left[ 1 + \frac{1}{V_m} \frac{\partial n_g}{\partial n_m} \right] \sum_i \sum_j (1 - X_{A_j}) \]

The BIPs between methanol and alcohols were adjusted using a simplex algorithm:

\[ OF = \frac{1}{N} \sum_i \left| X_{exp} - X_{calc} \right| \]

Measurement Equipment
Figure 1: Schematic illustration of the rig used for the measurements.

Specifications
- Titanium Rig – 300 ml
- Maximum working pressure: 700 bar
- Uncertainty
  - u(T): ± 0.5 K
  - u(P): ± 0.04 MPa

Methane in Pure Methanol and Ethanol

Figure 2: Methane solubility in methanol at (\(125\), \(273.15\), \(298\), \(350\) and \(330\) K. Data from Hong et al., 1987
3. Black Line: CPA-SRK72 model

Figure 3: Methane solubility in ethanol at various temperatures. (\(K\), \(238.15\), \(253.15\), \(263.15\)). \(T\) is \(238.15\ K\); \(253.15\ K\); \(263.15\ K\); \(288.15\ K\); CPA

- SRK72-model - Black line: calculated \(k_{ij}\) = -0.049; Dotted grey line: \(k_{ij}\) = 0.

Methane in Methanol and Ethanol Aqueous Solutions

Figure 4: Methane solubility in 50 wt% ethanol solution at \(T=273.15\ K\) and \(298.15\ K\). Lines: CPA-SRK72 model predictions. Black Line: \(k_{ij}\) = 0.052 prediction for 273.15 K and 298.15 K (respectively – high to low solubility).

Figure 5: Methane solubility in 70 wt% ethanolic solution at \(T=273.15\ K\). Lines: CPA-SRK72 model predictions. Grey Lines: \(k_{ij}\) = -0.049. Black Lines: \(k_{ij}\) = 0.052 prediction for 273.15 K and 298.15 K (respectively – high to low solubility).

Modelling Results

CH₄ = Methanol BIPs
\(k_{ij} = 0.13x^2 - 0.494x + 0.343\)

CH₄ = Ethanol BIPs
\(k_{ij} = 0.2875x^2 - 0.6175x + 0.281\)

Model Evaluation

The bubble points were calculated by CPA-SRK72 using the \(k_{ij}\) developed by Highghi et al. and the \(k_{ij}\) calculated utilizing the correlation developed using the data published by Wang et al. As can be clearly seen, the calculations significantly improve using the \(k_{ij}\) calculated using the above correlation.

Conclusion
The experimental data from this work was used to optimise the BIPs for methane-ethanol. This is due to the scarcity of such data, hence the model should be independently verified. The utilization of a concentration dependant BIP significantly improved the CPA-SRK72 calculations and predictions.