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Multiphase Flash with Hydrate Formation in Gas-Dominant Systems

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Abstract

Natural gas hydrates are solid crystals formed by water molecules (hosts) encasing gas molecules (guests) within cavities stabilized by hydrogen bonds. These hydrates can adopt various structures, primarily sI and sII. Understanding their phase diagrams is crucial, especially in oil and gas pipelines where blockages can occur. Constructing these diagrams elucidates the behavior of hydrates under specific conditions, particularly in gas-dominant systems, which involve complex experimentation and modeling, especially when the limited amount of water restricts hydrate formation. Thermodynamic modeling, based on statistical thermodynamics, links hydrate structures to their macroscopic properties. The van der Waals and Platteeuw theory is applied to describe hydrate phases (sI and sII), while the PC-SAFT and Peng-Robinson equations of state are employed for fluid phases, ensuring accuracy. The ice phase is treated as a pure solid, with its fugacity determined experimentally, aiding in the prediction of equilibrium across the phase diagram. By combining this with a multiphase flash algorithm and stability analysis, the thermodynamic model calculates isothermal-isobaric flashes through Gibbs energy minimization, subject to non-negativity constraints. The resulting phase diagrams were compared with literature data, revealing significant improvements in modeling accuracy compared to results obtained using PVTSim, a commercial simulator.
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Keywords

Multiphase Flash; Hydrates; Gas-Dominant System

Introduction

Natural gas hydrates are crystalline solids formed by water molecules (host) and small molecules (guest) present in the natural gas. Typical molecules include methane, ethane, and carbon dioxide [4]. They can exist in several structures; the main and most common ones being denoted in the literature as sI and sII. What differentiates an sI structure from an sII structure is the quantity of pentagonal and hexagonal faces, and consequently the number of water molecules per cavity. At low temperatures and high pressures (typical conditions for offshore production), water molecules bond through hydrogen bonds, and the guest molecule stabilizes the structure. Understanding the behavior of these systems in terms of phase diagrams is crucial, especially in pipeline obstruction during oil and gas production. Particularly in gas-dominated systems, where the amount of water is a limiting factor for the formation of these structures this understanding is even more necessary. Those conditions can be observed in the scenario of the Brazilian fields, where pressure and temperature conditions in deepwater oil exploration favor hydrate formation[5]. Measuring moisture content in these systems presents experimental complexity and modeling challenges. This present work aims to conduct hydrate formation simulations in gas-dominant conditions in different water concentrations, for a methane-water mixture, and compare the results with the commercial simulator PVTsim, as well as with experimental data [6].

Methodology

In this work, thermodynamic models were implemented for fluid phases (liquid and vapor), for solid phases (pure ice and r hydrate phase, considering only sI crystalline structure). Alongside an algorithm for multiphase flash calculation with stability analysis. The code was fully implemented in Python.

Hydrate Phase Modeling

For the hydrate phase, the Van der Waals and Platteeuw theory [7] is applied. In that theory the structure does not form due to the occupants; instead, it starts from a priori structure, and the occupation is modeled through Eq. (1). The occupation is simple, meaning only one type of occupant can exist per cavity, and there is no interaction between occupants of neighboring cavities.

$$\Delta\mu_W^{H-EL} = \mu_W^{H} - \mu_W^{EL} = k_B T \sum_i^n \nu_i ln(1 - \qquad (1)$$

Where $\Delta\mu_W^{H-EL}$ is the difference between the water chemical potential in the hydrate phase and in the hypothetical structure, μ_W^{H} is the water chemical potential in the hydrate phase, μ_W^{EL} is the water chemical potential in the hypothetical structure, ν_i is the ratio of type *i* cavities to water molecules and θ_{ij} is the occupancy fraction of type *i* cavities by molecules of type *j*. And, to calculate the difference in chemical potential between water in the unoccupied hypothetical structure and in the pure condition (ice or liquid) the Eq. (2) proposed by Saito et al. [8] is used.

$$\frac{\Delta\mu_W^{EL-PW}}{RT} = \frac{\Delta\mu_W^{EL-PW}(T_0,P_0)}{RT} + \frac{\Delta V_W^{EL-PW}}{RT}\Delta P + \frac{\Delta H_W^{EL-PW}}{RT}(-\frac{1}{T} + \frac{1}{T_0}) \qquad (2)$$

Where $\Delta\mu_W^{EL-PW}$ is the difference between the water chemical potential of the unoccupied hypothetical structure and in pure condition (ice or water), ΔV_W^{EL-PW} is the difference in the water molar volume in the unoccupied hypothetical structure and in pure condition (liquid and ice), ΔH_W^{EL-PW} is the difference in water molar enthalpy in the unoccupied hypothetical structure and in pure condition (liquid and ice) and $\Delta\mu_W^{EL-PW}(T_0, P_0)$ is the difference between the water chemical potential in the unoccupied structure and in the pure condition (ice or water) at an reference temperature and pressure.

Fluid Phase Modeling

The PC-SAFT and Peng Robinson equations of state were used for the fluid phases (liquid and vapor). The PC-SAFT (Perturbed Chain - Statistical Associating Fluid Theory) equation of state is composed of the sphere, chain, association, and dispersion terms [9], and the parameters for water (4C) and methane are from K. Nasrifar et al. [10]. The Peng Robinson equation of state has a modification in the attractive term only for the water component.

Ice Phase Modeling

The ice phase is modeled using experimental measurements of ice sublimation pressure and molar volume presented by Klauda and Sandler [11] as reference, where the water fugacity in the ice phase is calculated by Eq. (3).

$$f_w^I = P^{Sublim,I} \phi_w^{Sublim,I} exp\left(\frac{V_w^I}{RT}(P - P^{Sublim,I})\right) \qquad (3)$$

Where $P^{Sublim,I}$ is the ice sublimation pressure correlation, $\phi_w^{Sublim,I}$ is the water fugacity coefficient in the vapor sublimation condition and V_w^I is the water molar volume in the ice phase.

Multiphase Flash Calculation

The flash calculation allows determining the phase compositions and the relative fractions of each phase present in thermodynamic equilibrium by fixing two independent variables given the system global composition. With temperature and pressure specified, the solution is the Gibbs free energy global minimum. In this work, the methodology proposed by Gupta et al. [3] and Ballard [2] is followed, solving a minimization problem of total Gibbs free energy constrained to non-negative phase relative fractions, transforming the constrained minimization problem into an unconstrained minimization problem using the Lagrange multiplier method, solving it analytically, and defining the stability variable as Eq. (4).

$$\theta_j = \frac{\lambda_j}{N_s RT} \qquad (4)$$

Where λ_j represents the Lagrange multipliers and N_s is the number of moles in the system. Thus, Eq. (5) and Eq. (6) are derived.

$$\theta_j = ln\left(\frac{f_{i,j}}{f_{i,ref}}\right) \qquad (5)$$

$$\beta_j \theta_j = 0 \qquad (6)$$

If θ_j is equal to zero, the equality of fugacities applies, and phase *j* is in equilibrium with the other phases in the system. If β_j is greater than zero indicates the presence of the phase, if β_j is less than zero indicates an incipient phase. If θ_j is greater than zero, phase *j* is not present; that is, the fugacity of phase *j* will be higher than the fugacity of the reference phase. Based on the derived stability variable, a set of nonlinear equations similar to those of Rachford and Rice [12] is constructed, where the nonlinear algebraic equations Res_j that must be satisfied for each phase *j*, except for the reference phase, as proposed by Segtovich [1] in the algorithm, as Eq. (7).

$$Res_j = \sum_i^n \left(\frac{z_i(K_{i,j}e^{\theta_j} - 1)}{1 + \sum_{l \neq ref} [\beta_l(K_{i,l}e^{\theta_l} - 1)]} \right) = 0 \qquad (7)$$

Where $K_{i,j}$ is the distribution coefficient and $x_{i,j}$ the composition of component *i* in phase *j*.

Results and Discussion

Simulations were conducted for a methane-water mixture and compared to experimental data at pressures of 68.9 bar and 34.8 bar [6], as show in Figure 1. The graph depicts temperature against humidity. The simulations, which utilizes both equations of state models, exhibited good alignment with experimental data, indicating promise in predicting hydrate formation and humidity values in low water content.

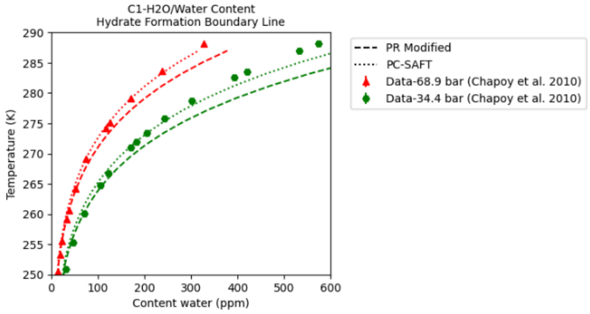

Figure 1. Calculated versus experimental data at 34.4 bar (34.4x10^5 Pa) and 68.9 bar (68.9x10^5 Pa), PC-SAFT and PR models.

Subsequently, the phase diagram was generated using the PVTsim software (Figure 2) and compared with the results obtained from the Peng Robinson (Figure 3) and PC-SAFT (Figure 4) models using the proposed algorithm. A retrograde dissociation prediction by PVTsim can be observed slightly above 100 bar, which is not seen in the other models. Additionally, both models with the algorithm proposed in this work have proven promising in describing the experimental data in those conditions.

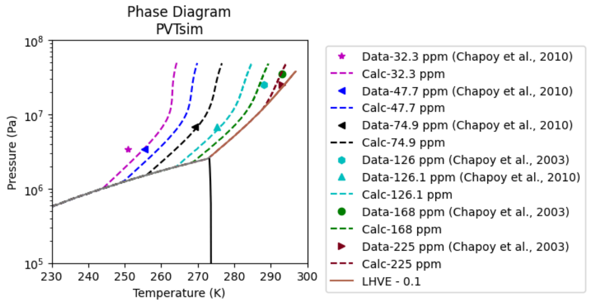

Figure 2. Phase diagram using the PVTsim software for different water contents from experimental data.

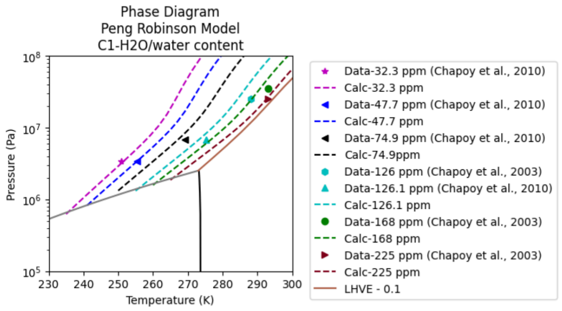

Figure 3. Phase diagram using the Peng Robinson Model for different water contents from experimental data.

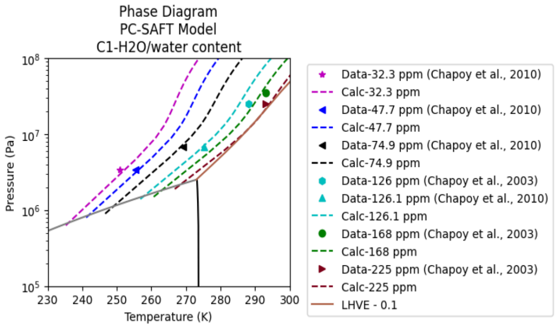

Figure 4. Phase diagram using the PC-SAFT Model for different water contents from experimental data.

Conclusions

The proposed approach and algorithm show promise in predicting water content in methane for gas-dominated systems. In the future, it is intended to perform the same simulations for more complex mixtures, such as CO_2, ethane and/or propane, for example, and compare these results with data from the literature to assess and improve the accuracy of the simulator calculations for gas-dominant systems.

Responsibility Notice

The authors are the only responsible for the paper content.

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