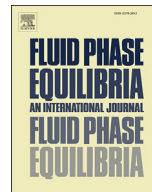




Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Phase diagrams for hydrates beyond incipient condition — Complex behavior in methane/propane and carbon dioxide/iso-butane hydrates

Iuri Soter Viana Segtovich ^a, Amaro Gomes Barreto Jr. ^a, Frederico Wanderley Tavares ^{a, b, *}^a Escola de Química, Universidade Federal do Rio de Janeiro, Rio de Janeiro, C.P.68542, Brazil^b Programa de Engenharia Química – COPPE, Universidade Federal do Rio de Janeiro, Rio de Janeiro, C.P. 68542, Brazil

ARTICLE INFO

Article history:

Received 31 October 2015

Received in revised form

11 January 2016

Accepted 3 February 2016

Available online xxx

Keywords:

Phase equilibria

Stability analysis

Hydrates

Phase diagram

ABSTRACT

We have recently developed an algorithm for multiphase equilibrium calculations and stability analysis involving hydrates. This algorithm allows phase equilibrium calculations in scenarios presenting different number of phases that may also be in distinct physical states.

Here, we present $P \times T$ phase diagrams calculated using our algorithm that involve mixed hydrates of natural gas beyond incipient condition and show complex behavior. Our phase diagrams show a global overview of the behavior of phase equilibrium involving hydrates in a mixture of water, methane and propane and in a mixture of water, carbon dioxide and iso-butane. We accomplish that using a global phase diagram in a wide range of pressure and temperature to show diverse phase equilibrium regions.

We present an approach to tune the Peng–Robinson equation of state to improve the calculations of the chemical potential of water in liquid state at high pressure and therefore, improve the prediction of the phase equilibrium between this phase and ice or hydrates, up to pressure conditions as high as 100 MPa.

Our calculations predict 3-phase equilibrium regions and 4-phase equilibrium univariant lines in binary hydrates of methane and propane and in binary hydrates of carbon dioxide and iso-butane. We use local phase diagrams highlighting details in regions with complex behavior of phase equilibrium to show how the phase boundary isopleths and univariant lines relate in a phase diagram for water, methane and propane.

Our calculations for a mixture of water, carbon dioxide and iso-butane predicts structural transitions occurring below the dew point line of the guest components, in a mixture with excess of guest components, and 5- phase equilibrium invariant point. We show equilibrium lines that present retrograde behavior in the phase diagram for this mixture.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

The knowledge on phase equilibrium behavior of hydrates is required in diverse situations: The most usual situations are plugging of pipelines during oil and gas production, in water or oil based drilling fluids and in inoperant lines [1]. Other recent applications of hydrate formation are energy production and logistics, respectively by means of exploration of methane reservoirs in permafrost or in deep seas, and by means of natural gas storage and transportation. In addition, separation processes explore hydrate phase

equilibrium behavior to separate greenhouse or industrial resource gases from air or from oil, and to separate water in desalination processes or from ionic liquids mixtures. Biotechnology explores the formation of clathrate hydrates in animal or plant tissues, gas hydrate formation in protein containing micellar solutions, applications in controlling enzymes in biological systems, in recovery of proteins, and in drug delivery systems [1–3]. $P \times T$ thermodynamic phase diagrams show the phases that are present at equilibrium for a mixture with known composition as function of the pressure and temperature condition. Natural gas hydrates are solid phases composed of water and some components from natural gas. These phases occur in some discrete different microscopic structures. For that, systems containing water and potentially hydrate forming components exhibit some complex behavior regarding phase equilibrium. Depending on pressure, temperature and composition

* Corresponding author. Departamento de Engenharia Química, Escola de Química, Universidade Federal do Rio de Janeiro, Cidade Universitária, CEP: 21949-900, Rio de Janeiro, RJ, Brazil.

E-mail address: tavares@eq.ufrj.br (F.W. Tavares).

of the stream, coexistence of different hydrate structures, ice and fluid phases occur.

We have recently developed an algorithm for multiphase equilibrium calculations and stability analysis involving hydrates. We present the details on this algorithm methodology and hydrate thermodynamic model elsewhere [4]. Here, we present details on complex $P \times T$ phase diagrams that we calculated using this algorithm for systems involving hydrates.

Sloan and coworkers [5–8] have also used multiphase algorithms to generate phase diagrams with calculations beyond initial hydrate formation conditions. However, these works had different focus: They presented $P \times x_1$ plots at different temperature conditions, a $P \times T$ plot in a small region for a mixture of ethane and propane, and some mixture triangular diagrams, for ternary guest mixtures, showing phase equilibrium regions depending on mole fraction of three guest components at several specifications of pressure and temperature. Here, we present a global overview of the behavior of phase equilibrium involving hydrates. We accomplish this using a global phase diagram in a wide range of pressure and temperature to show diverse phase equilibrium regions, and using some local phase diagrams highlighting details in regions with complex behavior of multiphase equilibria.

To improve phase equilibrium calculations, it is important to model adequately the chemical potential of all components in each phase. Here, to improve the calculations of phase equilibrium between liquid water and ice or hydrates, we tuned the Peng–Robinson equation of state to have a better modeling of the chemical potential of condensed water up to pressure conditions as high as 100 MPa.

2. Methodology

To calculate phase diagrams, we combine thermodynamic modeling of the relevant phases, a mathematical formulation of the phase equilibrium criteria, an algorithm to solve this formulation and a strategy for the elaboration of each lines that compose the diagrams.

2.1. Thermodynamic modeling of each phase

Microscopically, hydrates show a regular lattice composed of water molecules and cavities. Molecules with suitable size, called generally as guests, occupy these cavities. On this basis, van der Waals and Platteeuw [9] thermodynamic model provides the relation between molar fraction and fugacity of hydrate guests. Also, combining this model with a suitable model for the reference condition of the empty lattice of water, in an approach we discussed recently [4], we can obtain the fugacity of water in the hydrate phase and couple this modeling in generalized phase equilibrium calculations.

The relevant fluid phases in the systems studied here are vapor phases, aqueous liquid phases and liquid phase rich in non-polar components. We modeled these fluid phases using Peng–Robinson equation of state (PR-EoS), however to improve the calculations of the chemical potential of water in liquid state at high pressure we tuned the PR-EoS.

The key aspect of our approach is to use liquid molar volume data in the parameterization of the model. That is essential, because the partial derivative of chemical potential (μ_i) of a substance (i) with respect to pressure (P) at constant temperature (T) is its molar volume (v_i).

$$\left(\frac{\partial \mu_i}{\partial P}\right)_T = v_i \quad (1)$$

Therefore, when fitting the model parameter to saturation pressure data, a more adequate modeling of chemical potential near the saturation pressure curve is attained. However if the modeling of the molar volume is not adequate, the modeling of chemical potential becomes gradually worse at increasing pressure conditions.

Therefore, we focused on changing the co-volume parameter (b_w) of the equation of state, to which the liquid molar volume is expected to be most sensitive. On changing this parameter, the parameters associated with the attractive term (α_w) must change as well, in a simultaneous optimization procedure. We fitted the parameters of the modified-PR-EoS using experimental data of liquid molar volume and of saturation pressure between 0 °C and 100 °C. In this way, we generated an equation of state suitable to the conditions of the simulations of interest here.

Another solid phase relevant in the systems studied here is conventional ice. We modeled this phase using sublimation pressure as reference condition and Poynting correction [10].

To improve the prediction of the triple point of water, we refitted the parameters for the correlation of sublimation pressure of ice.

2.2. Thermodynamics of phase equilibrium

According to Duhem theorem [11], the specification of global mole composition and two independent thermodynamic properties is sufficient to specify a system equilibrium state. On specifying global mole composition, pressure and temperature, then the variables that characterize the state of equilibrium correspond to a minimum in total Gibbs energy [12]. In a multiphase equilibrium, according to Gibbs phase rule there is a maximum of phases that can coexist in a state of equilibrium, and this number is a function of the number of components (NC) in the system. The locus of coexistence for a number phases equal to NC or less phases is a region in the $P \times T$ plane, for NC+1 phases is a line, for NC+2 is a (P, T) point and more than that cannot coexist.

2.3. Algorithm

We assemble phase diagrams from recursive usage of a robust phase equilibrium algorithm capable of providing multiphase flash calculations coupled with incipient condition calculations. The algorithm that we used here is one we developed recently [4]. Our algorithm performs two types of calculations: P - T -flash calculations and incipient condition calculations accounting for an arbitrary number of phases simultaneously present in bulk amount. The first determines, at specified pressure, temperature, and composition, which are the phases that are present at equilibrium and what are their thermodynamic properties. It uses stability analysis to handle diverse scenarios regarding the number and physical states that are present at equilibrium from a set of modeled phases. The second determines the (P, T) points in the $P \times T$ phase diagram for a stream with known composition in which one or two specified phases are in incipient condition. These work according to three specifications. The first two, for one given phase as in incipient condition, determine pressure at a given temperature (T - β_1 -flash) or temperature at a given pressure (P - β_1 -flash). These correspond to points belonging to line segments of phase boundary curves. The third (β_1 - β_2 -flash) finds the pressure and temperature for the specification of two incipient phases. This corresponds to the point of intersection between two line segments.

2.4. Calculation of $P \times T$ phase diagrams

The phase diagram is composed of line segments that

Download English Version:

<https://daneshyari.com/en/article/4768217>

Download Persian Version:

<https://daneshyari.com/article/4768217>

[Daneshyari.com](https://daneshyari.com)