

A COMPARISON BETWEEN THE PHASE DIAGRAMS OF THE NATURAL HYDRATES USING THE PENG-ROBINSON AND SOAVE-REDLICH KWONG EQUILIBRIUM FORMULATIONS.

Mabelle Biancardi Oliveira

Pós-Graduação em Engenharia Metalúrgica-EEIMVR-UFF, Av. dos Trabalhadores 420 – Vila Sta. Cecília – 27255-125 – Volta Redonda – RJ

mabelle@metal.eeimvr.uff.br

José Adilson de Castro

Pós-Graduação em Engenharia Metalúrgica-EEIMVR-UFF, Av. dos Trabalhadores 420 – Vila Sta. Cecília – 27255-125 – Volta Redonda – RJ

adilson@metal.eeimvr.uff.br

Alexandre José da Silva

Pós-Graduação em Engenharia Metalúrgica-EEIMVR-UFF, Av. dos Trabalhadores 420 – Vila Sta. Cecília – 27255-125 – Volta Redonda – RJ

ajs@metal.eeimvr.uff.br

Alexandre Furtado Ferreira

Pós-Graduação em Engenharia Metalúrgica-EEIMVR-UFF, Av. dos Trabalhadores 420 – Vila Sta. Cecília – 27255-125 – Volta Redonda – RJ

furtado@metal.eeimvr.uff.br

Abstract: *One of the problems which occur in the petroleum extraction and transportation is the natural hydrates formation into the oil pipeline. In order to overcome this problem a strict control of the thermodynamics conditions is desirable. Therefore precise equilibrium data and predictions of the equilibrium variables have been searched. Usually, the equilibrium diagram is used to predict and determine the operational parameters of the equipments and processes set up involved on the extraction and transportation of petroleum industry. However, precise thermodynamics diagrams for a large range of operational conditions are not available and equilibrium relations based on several assumptions were proposed. This paper aims to verify the accuracy and compare two equilibrium relations commonly used to predict the thermodynamics of this system. In this study the Peng-Robinson and the Soave-Redlich-Kwong P-V-T relations are selected and compared with experimental results presented in the literature.*

Keywords: *Hydrates, solid-liquid equilibrium, phase diagram*

1. INTRODUCTION

The gas hydrates or simply hydrates are crystalline compounds ice-liked, formed for two or more components by means of an encapsulating structure. Its formation occurs when the water molecules through hydrogen bonding originate a crystalline lattice, that needs to include a large amount of molecules to stabilize its structure. The occluded molecules are generally gaseous into solid cavities. Depending mainly upon the occluded gaseous molecule size, the formation of two crystalline structures is commonly observed. These structures are termed structures I and II and represents the most common structure formed under oil pipelines operational conditions. The morphologies of common hydrates observed are presented in the Fig. 1. Recently, a third type was discovered and named H-structure by Bishnoi and Clarke (2001). These last one are formed by combining the two types of cavities (small and big occurring simultaneously at the same cavities) for similar structures.

The gas hydrates have been studied extensively for more than three decades taking into account formulations including its natural formation (Lerche and Bagirov, 1998), molecular structure (Freitas, 1990), physical and chemical properties (Edmonds et al, 1999), addition of inhibitors (Uchida et al, 2002), nucleation and growth (Bishnoi and Natarajan, 1996) and kinetic of dissolution (Kelkar et al, 1998). The pioneer reported work based on thermodynamic model was the van der Waals e Platteeuw (1949) that proposed a model for hydrates formation according to Langmuir gas adsorption to account for the natural hydrates thermodynamic properties. However, this model was only successfully applied to spherical molecules. Parrish e Prausnitz (1972), based on the van der Waals e Platteeuw (1949) model, established a methodology to determine the dissociation pressure of some gaseous hydrates using the function of Kihara for spherical nuclei and refined the theoretical results compared with experimental data. Munck *et al* (1988) developed a simplest equation for the Langmuir constant calculation as a function of temperature. With this relatively simple equation, they proved its functionality since the results obtained agreed satisfactorily with other results based on complex formulations, however this model is successfully applied for restrict temperature and pressure ranges. The present work aims to improve the previous model by taking into consideration the formulation of the Langmuir constants given by Munck *et al* (1988) into the van der Waals and Platteeuw (1949) by solving the phase chemical potentials. Besides, for the gaseous components mixture fugacity calculations, the constitutive Peng and Robinson

(1976) and Soave *et al.* (1990) equations were used. The numerical results were then confronted with experimental data and several operational conditions were investigated.



Figure 1 The classical hydrates formation structures, (a) structure I-type and (b) structure II-type.

2. METHODOLOGY

2.1. Model development

To determine the type of crystalline structure that will be formed and the hydrate dissociation pressure, the equality between the hydrate phase (μ_w^H) and the coexisting water-phase (μ_w^α) which could be ice, liquid water or either of chemical potential principle is invoked, as reads in Eq. (1)

$$\mu_w^\alpha = \mu_w^H \quad (1)$$

Thus, one can calculate each of the chemical potential for a given pressure and temperature which satisfy Eq. (1). The chemical potential of water in the phase α (μ_w^α) is given by:

$$\mu_w^\alpha = \mu_w^0 + RT \ln \left(\frac{f_w^\alpha}{f_w^0} \right) \quad (2)$$

where, μ_w^0 , R , T , f_w^α and f_w^0 are the chemical potential of water at the reference state, the universal gas constant, the operation temperature, the water fugacity in the phase α and the water fugacity in the pure state, respectively. The water chemical potential in the hydrate phase (μ_w^H) is given by Eq.(3):

$$\mu_w^H = \mu_w^\beta + RT \sum_i v_i \ln \left(1 - \sum_k \theta_{ki} \right) \quad (3)$$

where, μ_w^β , v_i , θ_{ki} represent the water chemical potential in the lattice, the number of cavities i -typed per water molecule in the lattice and the fraction of the k -type cavities occupied by gas i -component, respectively.

Therefore, by substitution of Eqs. (2) and (3) into (1), Eq.(4) is obtained:

$$\mu_w^0 + RT \ln \left(\frac{f_w^\alpha}{f_w^0} \right) = \mu_w^\beta + RT \sum_i v_i \ln \left(1 - \sum_k \theta_{ki} \right) \quad (4)$$

Ordering Eq. (4), is possible to appropriately arrange the difference term observed in the left-side of the Eq. (5), which represents the driving force for the hydrate formation:

$$\mu_w^\beta - \mu_w^0 = RT \ln \left(\frac{f_w^\alpha}{f_w^0} \right) - RT \sum_i v_i \ln \left(1 - \sum_k \theta_{ki} \right) \quad (5)$$

Dividing Eq. (5) by RT and applying the Gibbs-Duhem well-known thermodynamic relationship, Eq. (6) is obtained:

$$\frac{\Delta\mu_0}{RT_0} - \int_{T_0}^T \left(\frac{\Delta H_0 + \Delta C_p (T - T_0)}{RT^2} \right) dT + \int_{P_0}^P \frac{\Delta V_0}{RT} dP = \ln \left(\frac{f_w^\alpha}{f_w^0} \right) - \sum_i v_i \ln \left(1 - \sum_k \theta_{ki} \right) \quad (6)$$

where, $\Delta\mu_0$, ΔH_0 , ΔV_0 , ΔC_p , f_w^α , f_w^0 , v_i , θ_{ki} , \bar{T} and R represents the chemical potential differences, the molar enthalpy, the molar volume between water in “empty” lattice, the pure state of aggregation (liquid or solid) at the temperature 273,15 K, the calorific capacity, the water fugacity in the phase α , the water fugacity in the pure state, the number of cavities of type i per water molecule in the lattice, fraction of type k cavities occupied by gas component i , the average temperature between temperature T and the water reference temperature T_0 and the gases constant, respectively.

The equilibrium principle is satisfied when Eq. (6) is attained for a pair of T and P, which represents the equilibrium temperature and pressure respectively. The solution of Eq. (6) is performed by using an iterative procedure. In this work the iterative bisection method (Ruggiero and Lopes, 1996) was applied.

2.2 Calculation of the fugacity

The fugacity calculation in the gaseous mixture is computed according to Eq. (7):

$$F_i = y_i \phi_i P \quad (7)$$

where y_i , ϕ_i and P represent the molar fraction in the gas phase, the fugacity coefficient and the dissociation pressure, respectively.

The Peng-Robinson and the Soave-Redlich-Kwong (SRK) P-V-T relations were employed to the fugacity coefficient calculation. The general form of these relations is:

$$P = P_R + P_A \quad (8)$$

where P_R is a repulsion pressure and P_A an attraction one. It is important to observe that these equations differ only in the attraction pressure term, as shown in the Eqs. (9) and (10), referring to the Peng-Robinson and the Soave-Redlich-Kwong (SRK) expressions, respectively.

$$P_A = \frac{a(T)}{\underline{v}(\underline{v}+b)+b(\underline{v}-b)} \quad (9)$$

$$P_A = \frac{a(T)}{(\underline{v}(\underline{v}+b))} \quad (10)$$

Eq.(8) can be rewritten in its cubic form, as in Eq. (11) and (12), respectively for each method:

$$Z^3 - (1-B)Z^2 + (A-2B-3B^2)Z - (AB-B^2-B^3) = 0 \quad (11)$$

$$Z^3 - Z^2 + (A-B-B^2)Z - AB = 0 \quad (12)$$

where, Z is the compressibility factor and A and B are the parameters that are calculated according to Eqs. (13) and (14). These parameters are valid to both Eqs. (11) and (12).

$$A = \frac{aP}{RT^2} \quad (13)$$

$$B = \frac{bP}{RT} \quad (14)$$

Where, a depends simultaneously on the temperature and the acentric factor, as presented in Eqs. (15) to (18). The symbols P , R , T and b are used to represent the dissociation pressure, the gases constant, the input temperature in the numerical program and a mixture parameter defined by Eqs (19) and (20). The parameters a and b are defined by the mixture rule:

$$\begin{array}{ll} \text{Peng-Robinson} & \text{SRK} \\ a_i(T) = a_{ci}(T_{ci})\alpha(T_{ri}, \omega_i) & a_i(T) = a_{ci}(T_{ci})\alpha(T_{ri}, \omega_i) \end{array} \quad (15)$$

$$a_{ci}(T) = 0,45724 \frac{(RT_{ci})^2}{P_{ci}} \quad a_{ci}(T) = 0,42748 \frac{(RT_{ci})^2}{P_{ci}} \quad (16)$$

$$\alpha_i^{0,5} = 1 + (0,37464 + 1,54226\omega_i - 0,26992\omega_i^2)(1 - T_{ri}^{0,5}) \quad \alpha_i^{0,5} = 1 + (0,48 + 1,574\omega_i - 0,176\omega_i^2)(1 - T_{ri}^{0,5}) \quad (17)$$

$$a = \sum_i^N \sum_j^N y_i y_j (a_i a_j)^{0,5} (1 - k_{ij}) \quad a = \sum_i^N \sum_j^N y_i y_j (a_i a_j)^{0,5} (1 - k_{ij}) \quad (18)$$

$$b_i = 0,07780 \frac{RT_{ci}}{P_{ci}} \quad b_i = 0,08664 \frac{RT_{ci}}{P_{ci}} \quad (19)$$

$$b = \sum_i^N y_i b_i \quad b = \sum_i^N y_i b_i \quad (20)$$

Thus, it is possible to obtain the fugacity coefficient for each one of the existing components in the gas hydrates formation by the Peng-Robinson and SRK equations respectively, according to Eqs. (21) and (22):

$$\phi_i = \exp \left(-\ln(Z - B) + (Z - 1)B_i' - \frac{A}{2^{1,5} B} (A_i' - B_i') \ln \left(\frac{Z + (2^{0,5} + 1)B}{Z - (2^{0,5} - 1)B} \right) \right) \quad (21)$$

$$\phi_i = \exp \left(-\ln(Z - B) + (Z - 1)B_i' - \frac{A}{B} (A_i' - B_i') \ln \left(1 + \frac{B}{Z} \right) \right) \quad (22)$$

where A_i' and B_i' are defined by:

$$A_i' = \frac{1}{a} \left[2 a_i \sum_i^N y_i (a_i a_j)^{0,5} (1 - k_{ij}) \right] \quad (23)$$

$$B_i' = \frac{b_i}{b} \quad (24)$$

2.3 Calculation of the Langmuir constant

To calculate the hydrate chemical potential in the water phase is necessary to obtain the Langmuir constant (C_{ki}) by means of the determination of the A_{ki} and B_{ki} parameters at T (Munck *et al.* 1988), as shown in the Eq. (25):

$$C_{ki} = \left(\frac{A_{ki}}{T} \right) \exp \left(\frac{B_{ki}}{T} \right) \quad (25)$$

In order to determine the fractions occupied by each one of the gaseous component i into the cavities k . Eq. (26) is employed:

$$\theta_{ki} = \frac{C_{ki} f_{ki}}{\left(1 + \sum_j C_{ji} f_j \right)} \quad (26)$$

3. RESULTS AND DISCUSSIONS

The formulation used in this work was implemented in a computer code and aiming to validate the model and implementation the computational results were compared with the experimental data. Fig. 2 shows the model results based on Peng-Robinson and Soave-Redlich-Kwong (SRK) P-V-T relations compared with experimental data for pure methane. In Fig 2, the region left the equilibrium lines is the domain of hydrates formation while right side represents the operational conditions to avoid the hydrates formation. As can be observed, both relationships showed very close agreement with experimental data for low pressure and temperature. As pressure and temperature increased the Peng-Robinson relationship showed improved results when compared with SRK model. The reason for such behavior is the additional term considered in the Peng-Robinson equation for attraction pressure which is more severe at higher pressure, where the ideal gas behavior is not observed. In Fig 2, the green line represents the results calculated for the method of Peng-Robinson and the red line the method of SRK and the points the experimental data (John *et al.*, 1985). For pure methane only structure I hydrate is formed in the temperature and pressure range investigated due to the methane is a small molecule.

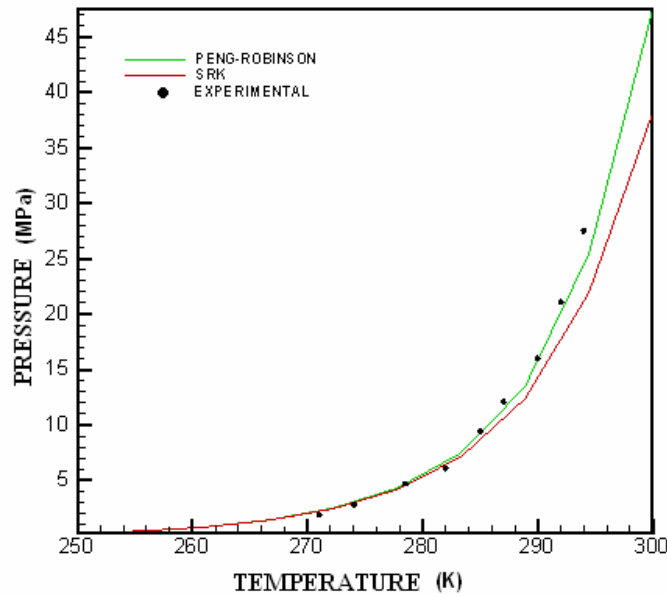


Figure 2 Hydrates formation of pure methane using Peng-Robinson and SRK PVT relations

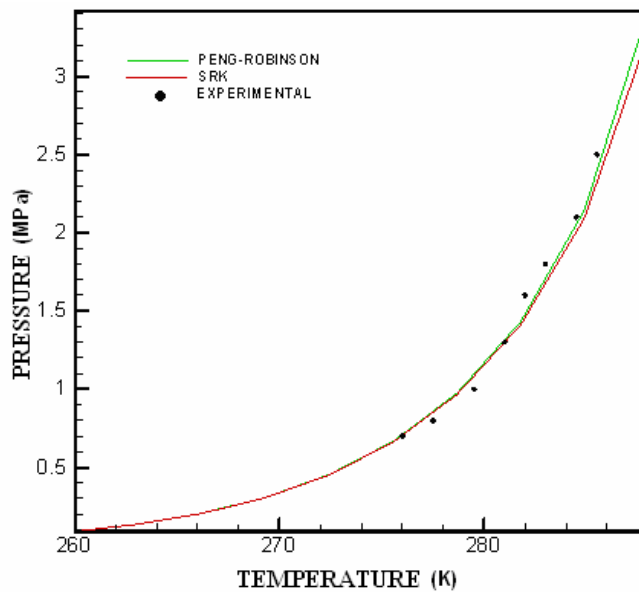


Figure 3 Comparison of hydrates formation of pure ethane

Figures 3 and 4 present equilibrium calculations for pure ethane and propane, respectively. In Fig. 3 the comparison of both relations are in close agreement as argued due to low equilibrium pressures. In Fig. 4, the agreement is closer since for propane the pressures are very low. Therefore, for pure components where the dissociation pressures are low both relationship are suitable for predict the thermodynamics conditions for natural hydrates formation, for both structure, as evidenced by ethane and propane, which forms structure I and II, respectively. As evidenced by the calculations supported by experimental data (Freitas, 1990), higher equilibrium pressures indicated that the Peng-Robinson relation is more accurate for methane molecules.

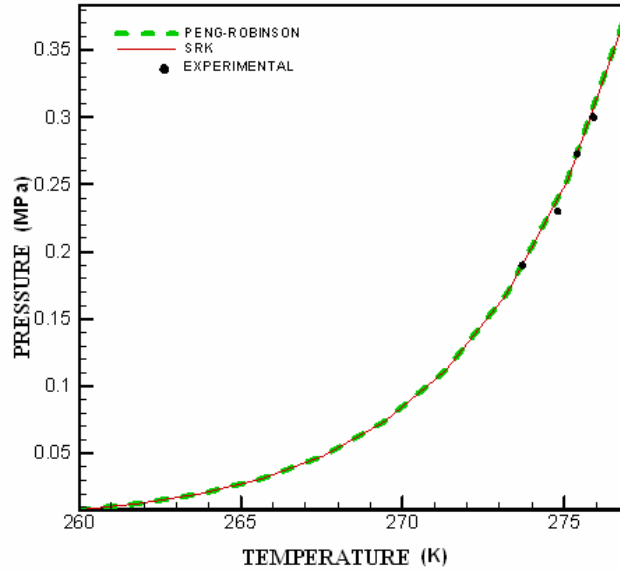


Figure 4 Hydrates formation equilibrium for pure propane

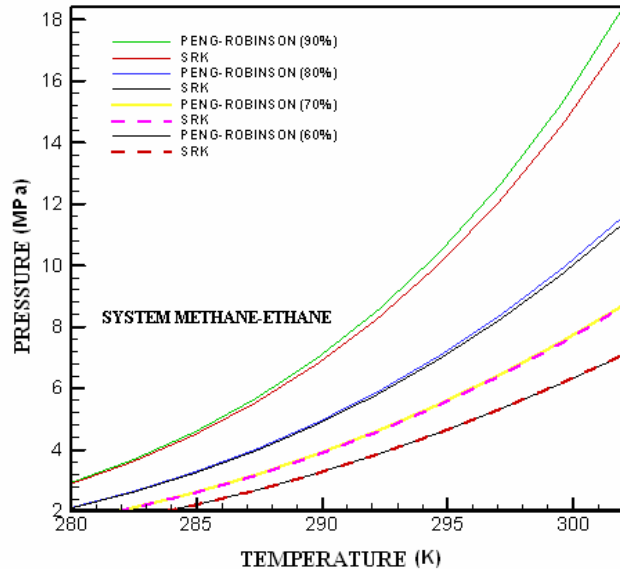


Figure 5 Hydrates formation from methane-ethane using Peng-Robinson and SRK PVT relations

The model was applied to investigate the hydrates formation from gas mixtures. Fig. 5 compares the Peng-Robinson and SRK relations for equilibrium calculations of system methane-ethane mixture. Even though the hydrate formation is from different gas mixture the same behavior was observed, i.e. for high pressure the Peng-Robinson relation differs significantly of the predictions of SRK while for low pressure no difference was predicted, which leads to conclusion that for low pressures both relations are suitable for numerical predictions.

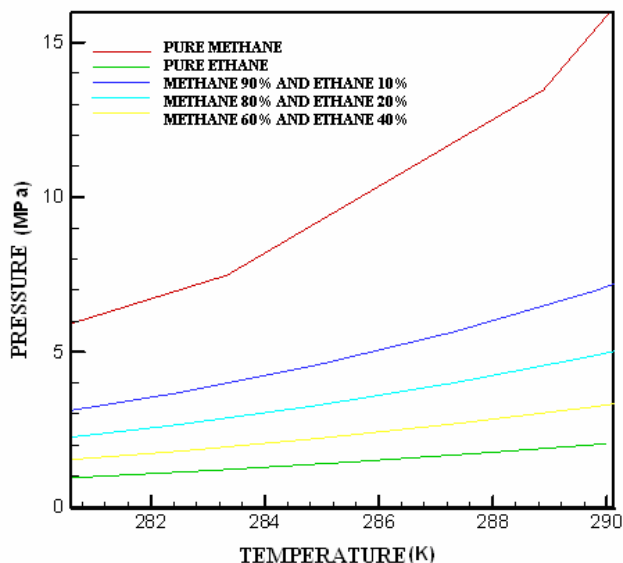


Figure 6 Comparison of hydrates formation from pure methane, pure ethane and mixture methane-ethane using the equation Peng-Robinson relationship

Figure 6 presents calculation results of hydrates formation for methane ethane system compared with the pure gas. As observed, ethane equilibrium is reached in lower pressures while methane is formed at higher pressure. However for gas mixture the, the equilibrium are not a simple linear interpolation, since the interactions molecule-molecule are relevant when the amount of the solute gas increases indicating non-ideal mixture for the system methane-ethane.

4. CONCLUDING REMARKS

A computational code based on the Peng-Robinson and SRK relations was implemented and validated by comparison with experimental data. The model solves the chemical potential equality based on the bisection method and thermodynamic data for gas and liquid phases were collected from the literature. A very good agreement of the numerical predictions and experimental data was obtained for low pressures in all system investigated. For higher pressures the Peng-Robinson relationship presented superior comparison with all experimental data analyzed. The model was applied to investigate gaseous mixture in several hydrates formation conditions. Simulations results indicated that hydrates of methane are formed for pressure above 5MPa, which is common operational pressure in oil industry. Therefore, lower and higher temperature is safety operational conditions for the equipment operation.

5. ACKNOWLEDGEMENTS

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