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PHASE EQUILIBRIA MODELLING OF GAS HYDRATES WITH MIXTURE OF INHIBITORS

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Abstract. *In this study, hydrates formation conditions were modelled for complex multicomponent systems, including the presence of thermodynamic inhibitors mixtures. A robust flash algorithm was developed in order to reproduce those hydrates formation conditions. The model consists on a statistical thermodynamic approach for the hydrate phase based on the van der Waals and Platteeuw theory and on the Cubic Plus Association (CPA) equation of state for the fluid phases. Predictions of the developed method have been compared with experimental data from the open literature and provided an acceptable agreement.*

Keywords: *Clathrate Hydrates, Phase Equilibria, Flash Calculation, Cubic-Plus-Association (CPA), Inhibitors Mixture*

1. INTRODUCTION

Gas hydrates are crystalline complexes, where water molecules are linked through hydrogen bonding and create interstitial cavities that can enclose guest molecules, typically light gases and hydrocarbons.

Oil and gas production lines usually contains light hydrocarbons, non-combustibles (i.e., carbon dioxide and nitrogen) and produced/formation water. The combination of low temperatures, high pressures, light components and water suggests that oil and gas pipelines can operate within the hydrate stable region (Sloan et al., 2010).

In a research with 110 energy companies, flow assurance was listed as the major technical problem in offshore energy development and the formation of hydrates the main problem in the oil and gas transportation at production operations. Indeed, hydrates can seriously affect production operations by either reducing or causing the complete interruption of those operations due to their accumulation and eventual blockage of flowlines. Moreover, hydrate plug remediation is not only costly, but develops into potentially hazardous conditions (Sloan et al., 2010).

Several methods are available to prevent or suppress hydrate occurrence. The injection of thermodynamic hydrate inhibitors (THIs), such as alcohols and glycols, is typically an option, as these chemicals tie-up water and dislocate the hydrate formation conditions to lower temperatures and higher pressures. These inhibitors are soluble in the aqueous phase and they inhibit hydrates by cross associating with water molecules, impeding the formation of hydrogen bonds between water molecules and thus preventing the formation of the hydrate structure (Sloan and Koh, 2008).

In general, produced water contains some quantities of salts, reducing the propensity of gas hydrate formation. In cases where the inhibition effect of the produced saline water is not effective enough to avoid hydrate formation, thermodynamic inhibitors could be injected into the pipelines, resulting in a system containing both salts and inhibitor. Accurate knowledge of gas hydrate dissociation conditions in the presence of aqueous solutions of salts and/or thermodynamic hydrate inhibitors is therefore crucial to prevent gas hydrate formation.

This article presents a modelling study for three-phase equilibrium conditions of liquid water-hydrate-vapour (L_w-H-V), liquid water-hydrate-condensate gas (L_w-H-L_g) and ice-hydrate-vapour (I-H-V) for different gases (methane,

ethane, propane, isobutane, carbon dioxide and nitrogen) and their mixture with and without thermodynamic inhibitors (ethanol, methanol, monoethylene glycol and sodium chloride). The applied model uses the CPA EoS (Kontogeorgis et al., 1996) for the fluid phases and the van der Waals and Platteeuw solid solution model (1959) for the hydrate phase.

2. THERMODYNAMIC MODELLING

During the calculation of a thermodynamic equilibrium for a closed system, three fundamental conditions must be met:

1. Equality of temperature in all phases;
2. Equality of pressures in all phases;
3. Equality of chemical potential for each substance in each phase.

In some cases, it is more convenient to work with the concept of fugacity instead of chemical potential, and as well as the chemical potential in the thermodynamic equilibrium condition, the fugacity of each substance in each phase must be equal. This concept is very important in the model developed in this work because it was initially adopted a flash calculation to determine the composition of each phase, and this isofugacity condition was implemented as the convergence criteria for the flash.

The fugacities of the components in the fluid phases were calculated by the Cubic-Plus-Association (CPA) equation of state (Kontogeorgis et al., 1996), the hydrate phase was modelled according to the model proposed by van der Waals and Platteeuw (1959).

2.1 Cubic-Plus-Association (CPA)

The CPA model is an EoS that combines the simplicity of a cubic EoS (the SRK equation) and the association (chemical) term from the Wertheim theory, as in SAFT. The SRK model accounts for the physical interactions between the molecules. The association term takes into account the specific site-site interaction due to hydrogen bonding between like molecules (self-association) and unlike molecules (cross-association or solvation). Polarity and quadrupolar interactions are not explicitly taken into consideration (Kontogeorgis et al., 2006).

The Cubic-Plus-Association (CPA) was initially presented by Kontogeorgis et al. (1996) and it can be expressed in terms of pressure as:

$$P = \frac{RT}{v_m - b} + \frac{a}{v_m\left(v+b\right)} - \frac{1}{2}\frac{RT}{v_m}\left(1+\rho\frac{\partial \ln\left(g\right)}{\partial \rho}\right)\sum_i x_i \sum_{A_i}\left(1-X_{A_i}\right) \tag{1}$$

where R is the universal constant of the gases, T is the temperature, v_m is the molar volume, a is the temperature-dependent SRK (Soave-Redlich-Kwong) energy parameter, b is the SRK co-volume parameter, g is the radial distribution function, A_i denotes association site A on component i, x_i is the mole fraction of component i, and X_{Ai} is the fraction of the sites, type A on component i, not bonded to other sites.

The right hand side of Eq. (1) is a sum of three terms. The first two terms are identical to the SRK equation of state, and they are responsible for the physical part of the CPA, (i.e., describing the fluid as a collection of free particles and with a weak attraction between them) (Kontogeorgis and Folas, 2010).

The third term in the CPA equation (Eq. (1)) is the association contribution, which depends on the interaction energy between hydrogen bond-forming molecules. Since the association term is based on Wertheim's first-order thermodynamic perturbation theory (TPT-1), as presented by Chapman et al. (1990), the assumptions inherent in the SAFT approach apply to CPA. In particular, the activity of each bonding site is assumed independent of the other bonding sites on the same molecule. Moreover, one site on a molecule cannot bond simultaneously to two sites on a different molecule and there is no double bonding between two molecules (Kontogeorgis et al., 2006).

The attractive parameter for inert compounds, a, is given by

$$a = a_0\left[1+c_1\left(1-\sqrt{T/T_c}\right)\right]^2 \tag{2}$$

where a_0 and c_1 are pure component parameters and T_c is the critical temperature. Usually, these pure components parameters are optimized by fitting the model to experimental vapor pressures and saturated liquid densities of the pure component. In the present work, they were taken from Tsivintzelis et al. (2011). In the case of mixture, it is necessary to introduce mixing rules. The mixing and combining rules for a and b are the classical van der Waals equations

The calculation of the X_{Ai} depends on the association scheme that is going to be adopted in the model and it must be consistent with the geometry and the distribution of charges of the involved molecules. This scheme basically presents the positives and negatives sites in each molecule and to what sites each of them can associate. Following the nomenclature presented, for instance, in Kontogeorgis and Folas (2010), in this work it has been adopted the 4C-scheme

for water and MEG, and the 2B-scheme for ethanol and methanol. For carbon dioxide, it is assumed that it only cross-associates, with two electron accepting sites. All the other gases are non-associative compounds.

Once determined the association scheme, the values of X_{Ai} are calculated by the set of implicit equations given by:

$$X_{A_i} = \frac{1}{1+\frac{1}{v_m}\sum_j x_j \sum_j X_{B_j} \Delta^{A_i B_j}} \tag{3}$$

where B_j indicates summation over all sites.

The Δ^{AiBj} is the association strength between site A on molecule i and site B on molecule j, and it also depends on the structure of the molecule and the number and type of sites. The association strength can be estimated according the following equation:

$$\Delta^{A_i B_j} = g\left(v_m\right)\left[exp\left(\frac{\varepsilon^{A_i B_j}}{RT}\right)-1\right] b_{ij} \beta^{A_i B_j} \tag{4}$$

ε^{AiBj} and β^{AiBj} are the association energy and association volume, respectively, between site A on molecule i and site B on molecule j. The CR-1 combining rules were implemented to the consideration of cross-association and a modified combining rule mCR-1 was applied for carbon dioxide with water, alcohols and glycols.

Kontogeorgis et al. (1999) proposed a simpler expression for g (sCPA):

$$g = \frac{1}{1-1.9\frac{B}{4v_m}} \tag{5}$$

The main reason of utilizing the CPA equation in this model relies in the fact that the molecules of components studied (water, methanol, ethanol, MEG, carbon dioxide) can associate between themselves and this influences the hydrate equilibrium conditions. This effect have influence in the fugacity of the gas phase, in the solubility of gas in the liquid phase, and in the activity of water in the liquid phase. All of those three quantities (calculated solely from CPA) are important in our model, as will be shown next.

2.2 The van der Waals and Platteeuw (vdWP) model

The hydrate phase is modelled using the solid solution of van der Waals and Platteeuw (1959), as implemented by Parrish and Prausnitz (1972). The hydrate phase model is based on the thermodynamic equilibrium, which means equality of temperatures, pressures and fugacities.

In this theory, hydrate is designed as a set of cavities formed by water molecules. It is considered that there is no deformation of these cavities due to the occlusion of the guest molecule and that occluded molecule only interacts with the water molecules of the corresponding cavity. The molecules occluded in neighboring cavities do not interact.

The vdWP theory computes the change in the chemical potential of water as a result of the guest molecule inclusion in the hydrate crystal structure. One can write this change in chemical potential as

$$\Delta\mu_W^{\beta-H} = \mu_W^{\beta} - \mu_W^{H} \tag{6}$$

Here, β is a hypothetical empty water crystal structure with no guest molecules, used for calculation convenience as a reference state. According to vdWP theory, applying some methods of statistical mechanics and appropriate idealizations is possible to write the variation of chemical potential as a result of the occupancy of the guest molecules as

$$\Delta\mu_W^{\beta-H} = RT\sum_k \upsilon_k \ln\left(1-\sum_i Y_{ik}\right) \tag{7}$$

where υ_k is the number of cages of type k per water molecule in a unit cell of the crystal and Y_{ik} is the probability that a molecule of the species i to occupies a cage of type k. This probability is given by the following equation:

$$Y_{ik} = \frac{C_{ik} f_i}{1 + \sum_i C_{ik} f_i} \tag{8}$$

Here, f_i is the fugacity of the species *i*. The constants C_{ik} are the so-called Langmuir constants, a terminology derived from an analogy with the theory of gas adsorption on solid surfaces. According to van der Waals and Platteeuw (1959), it can be calculated as

$$C_{ik} = \frac{4\pi}{kT} \int_0^{R_k - a_i} \exp\left(-\frac{w_{ik}(r)}{kT} \right) r^2 dr \tag{9}$$

In the equation above, R_k is the mean radius of the cavity *k*, a_i is the radius of the guest molecule *i* and $w_{ik}(r)$ is the potential energy of the interaction between the specie *i* and the layer formed by the water molecules in the cavity *k*. Here there is the assumption that the energy of the interaction depends only on the distance *r* from the center of the cavity to the center of guest molecule. In this work, a spherically symmetrical interaction potential, the Kihara potential (Mckoy and Sinanoglu, 1963), has been assumed.

2.3 Debye-Huckel

In the presence of electrolytes, the fugacity of the non-electrolytic compounds is calculated by combining the equation of state with the electrostatic contribution of Debye- Hückel for taking into account the effect of the salt (Aasberg-Ptersen et al, 1991).

$$\ln \phi_i = \ln \phi_i^{EOS} + \ln \gamma_i^{EL} \tag{10}$$

where ϕ_i is the fugacity coefficient of component *i*, ϕ_i^{EoS} is the fugacity coefficient of component *i* neglecting the electrostatic effect calculated by the CPA and γ_i^{EL} is the contribution of the electrostatic term. Using the Debye-Huckel activity coefficient, the second term in Eq. (10) would be (Aasberg-Petersen, 1991):

$$\ln \gamma_i^{DH} = \frac{2AM_m h_{is}}{B^3} f\left(BI^{1/2}\right) \tag{11}$$

Here, M_m is the salt-free mixture molecular weight and h_{is} is the interaction coefficient between the dissolved salt and a non-electrolytic compound, $f(BI^{1/2})$ is a function dependent of the ionic strength, *A* and *B* are calculated parameters. For more details about h_{is} calculation, please see Tohidi (1995).

3. CALCULATION METHOD

The algorithm for hydrate dissociation pressure calculation used is similar to that presented by Parrish and Prausnitz (1972). Initially, it was developed a two-phase flash calculation, utilizing the CPA Eos for the description of both phases. The fugacity coefficients of the non-electrolyte compounds given by the CPA Eos were combined to the electrostatic contribution of Debye- Hückel, according to the Eq. (10) for taking into account the effect of the salt. The binary interaction parameters of the CPA (k_{ij}) were obtained by fitting the model to experimental vapour-liquid equilibrium pressures data from literature and are provided in Tab. 1.

Table 1. Optimized binary interaction parameters (k_{ij}) for CPA EoS.

Binary System	Temperature range (K)	Reference	k_{ij}	AAD (%)
$CH_4 + H_2O$	275-313	Chapoy et al. (2004a)	$0.0031003 \cdot T - 0.92164$	4.02
$C_2H_6 + H_2O$	274-343	Mohammadi et al. (2004)	$0.001285 \cdot T - 0.337458$	1.97
$C_3H_8 + H_2O$	277-3686	Chapoy et al. (2004b)	$0.001422 \cdot T - 0.397035$	6.23
$CO_2 + H_2O$	278-318	Valtz et al. (2004)	$0.001482 \cdot T - 0.340089$	7.90
$N_2 + H_2O$	274-363	Chapoy et al. (2004c)	$0.004226 \cdot T - 1.421138$	2.28
$CH_3OH + H_2O$	308-338	McGlashan and Williamson (1976)	$-5.9357 \cdot 10^{-5} \cdot T - 3.6723 \cdot 10^{-2}$	2.67

$C_2H_5OH + H_2O$	303-363	Pemberton and Mash (1978)	$0.000404 \cdot T - 0.176037$	8.45
$C_2H_6O_2 + H_2O$	373-470	Kamihama et al. (2012)	$0.000518 \cdot T - 0.226980$	4.39
$CH_4 + CH_3OH$	200-330	Hong et al. (1987)	$3.4907 \cdot 10^{-5} \cdot T + 3.5810 \cdot 10^{-2}$	4.57
$CH_4 + C_2H_5OH$	313-333	Cai et al. (2015)	$-3.8268 \cdot 10^{-5} \cdot T + 2.1977 \cdot 10^{-2}$	1.42
$CH_4 + C_2H_6O_2$	283-303	Wang et al. (2003)	$-0.001668 \cdot T + 0.263366$	2.85
$C_2H_6 + CH_3OH$	240-298	Zeck et al. (1986)	$0.0001224 \cdot T + 0.0143678$	6.31
$C_2H_6 + C_2H_5OH$	313-333	Suzuki et al. (1990)	$7.3888 \cdot 10^{-5} \cdot T - 1.7467 \cdot 10^{-2}$	13.73
$C_2H_6 + C_2H_6O_2$	283-303	Wang et al. (2007)	$0.000914 \cdot T - 0.113106$	9.72
$C_3H_8 + CH_3OH$	313-327	Joung et al. (2004)	$0.00184984 \cdot T - 0.55002008$	11.74
$C_3H_8 + C_2H_5OH$	313-349	Joung et al. (2004)	$-5.19866 \cdot 10^{-5} \cdot T + 3.89782 \cdot 10^{-2}$	5.27
$C_3H_8 + C_2H_6O_2$	298-398	Jou et al. (1991)	$0.00018529 \cdot T + 0.04026127$	1.97
$C_4H_{10} + CH_3OH$	298-323	Kretschmer e wiebe (1952)	$0{,}00012128 \cdot T - 0{,}01190412$	0.20
$C_4H_{10} + C_2H_5OH$	283 – 323	Kretschmer e wiebe (1951)	$0{,}0002292 \cdot T - 0{,}01190412$	0,32
$CO_2 + CH_3OH$	230-330	Hong and Kobayashi (1998)	$-0.00011456 \cdot T + 0.07878186$	7.70
$CO_2 + C_2H_5OH$	288-323	Dalmolim et al. (2006)	$-1.421583 \cdot 10^{-4} \cdot T + 1.8494205 \cdot 10^{-1}$	2.56
$CO_2 + C_2H_6O_2$	288-318	Gui et al. (2011)	$-0.00036073 \cdot T + 0.20389652$	3.40
$N_2 + CH_3OH$	223-300	Weber et al. (1984)	$5.765040 \cdot 10^{-5} \cdot T + 5.23901 \cdot 10^{-2}$	2.34
$N_2 + C_2H_5OH$	298-398	Fischer et al. (2001)	$-0.00019172 \cdot T + 0.05462973$	2.96
$N_2 + C_2H_6O_2$	323-398	Zheng et al.(1998)	$0.00107242 \cdot T + 0.07301257$	41.31

The flash calculation was used to obtain the input required for the van der Waals and Platteeuw model. In a very summarized way, this model solves vdWP model for an equilibrium pressure at a specified temperature.

The properties regarding the structure of hydrate were taken from Sloan and Koh (2008). The Kihara potential parameters for the description of the Langmuir adsorption constants have been attained by fitting the model to hydrate dissociation pressures of pure gas hydrates at the three phase equilibrium region (L_w-H-V). The optimized Kihara parameters are provided at Tab. 2.

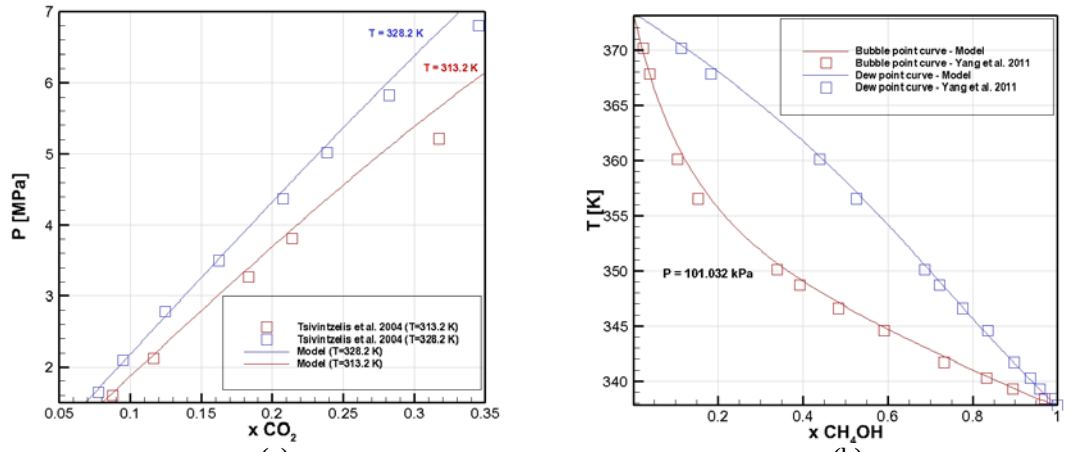
Table 2. Optimized Kihara parameters.

Hydrate former	ε/k (K)	σ (Å)	a (Å)
CH_4	151.96190887	3.38301732	0.23905350
C_2H_6	178.16841087	3.32970989	0.56927722
C_3H_8	238.99999900	3.30099952	0.68299991
CO_2	179.28763607	2.79392769	0.78995436
N_2	148.15626774	3.29872481	0.29354974

4. RESULTS AND DISCUSSION

To validate the modelling procedure adopted in this study, the results were compared to previously reported data and to an existing software, the CSMGem developed by the Center for Hydrate Research of Colorado School of Mines.

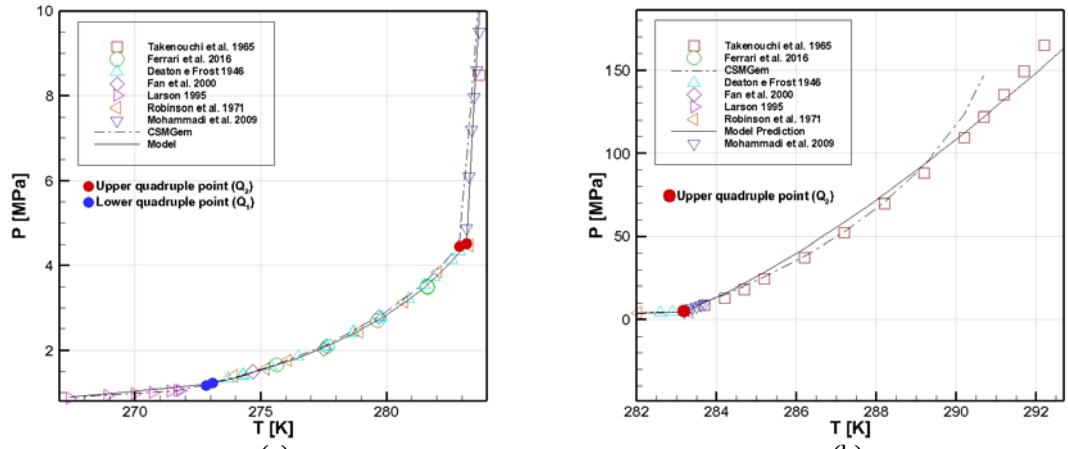
Initially, a validation of the two-phase flash calculation will be presented through vapour-liquid equilibrium (VLE) calculation and prediction of solubility of gas in liquid. Fig. 1 shows the solubility of carbon dioxide in ethanol and the VLE of a mixture of methanol and water. The experimental data presented in this figure are different from the data that were used to obtain the binary interaction parameters. As can been seen, there is a good accordance between the data reported in the literature and the developed model. The average absolute deviation (AAD) calculated for the solubility of the carbon dioxide in ethanol was 3.37% and for the VLE of methanol and water was 4.11%.



(a) (b)

Figure 1. a) Solubility of CO_2 in ethanol. b) VLE of methanol and water.

After the validation of the two-phase flash, were performed numerical simulations involving hydrates. In Fig. 2 it is presented all the data measured for the carbon dioxide hydrate system without any inhibitor. The first graphic (a) presents the L_w-H-V, I-H-V and L_w-H-L_g equilibriums and the second (b) emphasizes the L_w-H-L_g equilibrium. There is a good agreement between the previous studies, the model developed in this work and the CSMGem, suggesting the consistency of the thermodynamic modelling adopted. The model and the CSMGem presented an average absolute deviation (AAD) in the L_w-H-V equilibrium of 1.40% and 1.48%, respectively. For the I-H-V equilibrium, the AAD calculated for the model was 6.84% and 1.91% for the CSMGem. In the L_w-H-L_g equilibrium the model and the CSMGem presented an AAD of approximately 10%. It is also important to emphasize that the CSMGem was not able to calculate pressures above 1,500 bar.



(a) (b)

Figure 2. Carbon dioxide hydrate phase equilibria conditions in pure water. a) L_w-H-V, I-H-V and L_w-H-L_g equilibria. b) L_w-H-L_g equilibrium.

The natural gas found in the reservoirs is a mixture of different compounds, predominantly of light hydrocarbons. With the intention of approximating of the natural gas observed in nature, gas mixtures were implemented in the model. The next results that are going to be presented are related to gas mixtures hydrates with or without the presence of thermodynamic inhibitors.

In Fig. 3(a) and 3(b), it is possible to observe the L_w-H-V equilibrium for gas mixtures of methane and carbon dioxide with MEG and without MEG, respectively. The composition of the gas mixture in Fig. 3(a) is 90% methane and 10% ethane; Fig 3(b) presents a higher concentration of carbon dioxide (20%) and also MEG (10% mass fraction) as a hydrate inhibitor. The AAD presented by the model and the CSMGem in Fig. 3(a) were 0.70% and 2.03%, respectively. In Fig. 3(b) the AAD presented by the model was 1.01% and 1.08% by the CSMGem.

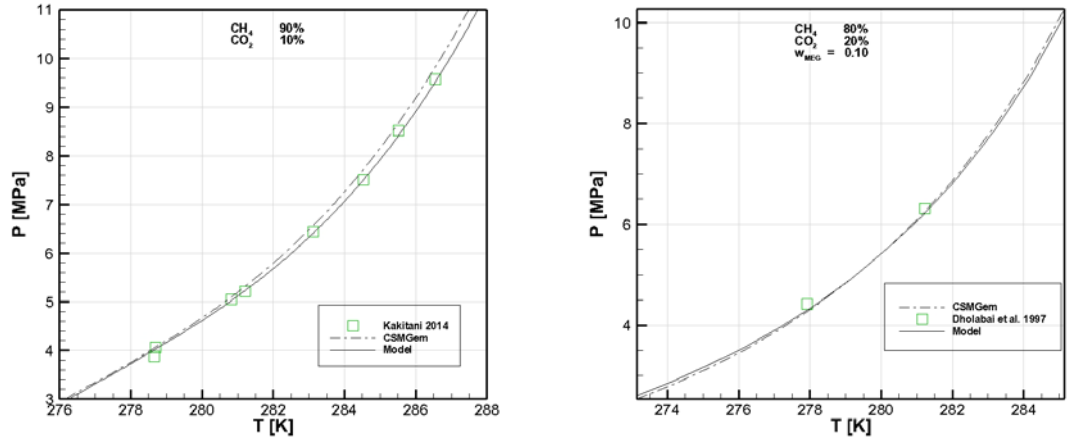


Figure 3. Hydrates equilibrium conditions for mixtures of methane and carbon dioxide (L_w-H-V). a) Without inhibitor. b) With 10% mass fraction of MEG.

Figure 4 shows hydrate formation conditions for ternary gas mixtures. In Fig. 4(a) it is presented L_w-H-V equilibrium conditions for a gas mixture containing 94.97% of methane, 5% of carbon dioxide and 0.03% of nitrogen, presenting an AAD of 0.66% by the model and 3.75% by the CSMGem. In Fig. 4(b) it is possible to observe the L_w-H-V equilibrium for a mixture of 91.96% of methane, 5.13% of ethane and 2.91% of propane with and without the inhibition effect of a 10% solution of MEG in mass fraction. As can be noticed in Fig. 4(b), the presence of a thermodynamic inhibitor causes the hydrate equilibrium curves to be displaced to higher pressures for the same equilibrium temperature if compared with the system without inhibitor. The AAD presented by the model and by the CSMGem for the system without inhibitor were 3.02% and 4.41%, respectively. The AAD calculated for the system with the presence of MEG was 5.03% for the model and 6.34% for the CSMGem.

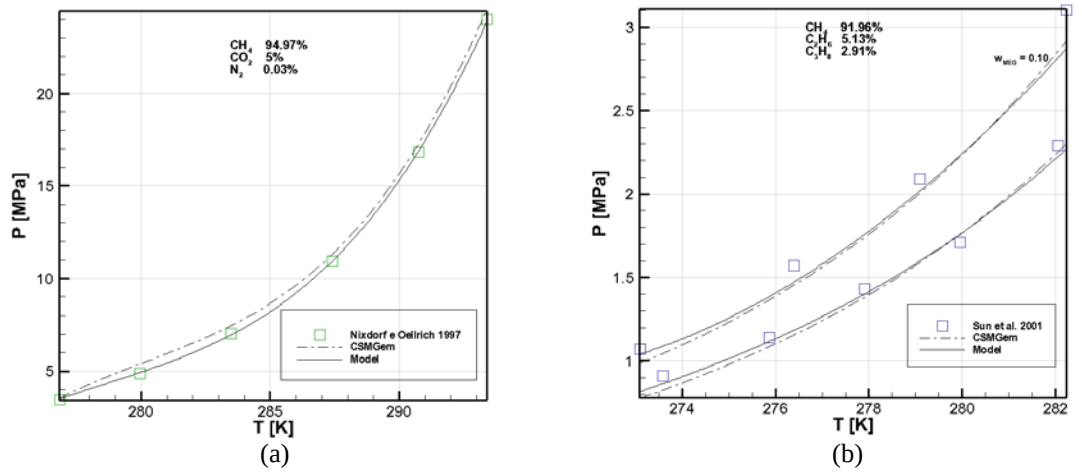


Figure 4. Hydrates equilibrium conditions for mixtures of ternary gas mixtures (L_w-H-V). a) Methane, carbon dioxide and nitrogen. b) Methane, ethane and propane with and without MEG (10% mass fraction).

Table 3 shows the hydrate formation conditions for a mixture of methane, carbon dioxide and propane in the presence sodium chloride. The composition of the mixture and the percentage of the inhibitor change along the table.

Table 3. Hydrate formation conditions for a mixture of methane, carbon dioxide and propane in the presence of methanol and sodium Chloride.

T (K)	$x_{methane}$	x_{CO2}	$x_{Propane}$	x_{NaCl} **(wt%)**	P_{exp} **(MPa)**	P_{Model} **(MPa)**	P_{CSMgem} **(MPa)**	AAD_{Model}	AAD_{CSMGem}
280.78	0.82	0.16	0.02	0.05000	3.269	3.404	3.187	4.12	2.50
285.19	0.80	0.18	0.02	0.0500	6.025	6.117	5.811	1.52	3.54

288.03	0.79	0.19	0.02	0.0500	9.849	9.810	9.407	0.40	4.49
277.73	0.79	0.19	0.02	0.1000	2.876	3.247	2.820	12.91	1.94
282.36	0.80	0.18	0.02	0.1000	5.633	5.803	5.216	3.02	7.40
274.25	0.78	0.20	0.02	0.2000	3.728	3.690	3.132	1.02	15.99
276.9	0.78	0.20	0.02	0.2000	5.286	5.202	4.598	1.60	13.01
279.97	0.80	0.18	0.02	0.2001	8.874	8.152	7.448	8.14	16.07
								4.09	8.12

Source: Experimental data from Bishnoi and Dholabhai (1999).

In Table 4, it is also possible to observe the hydrates formation conditions for mixtures of methane, carbon dioxide and propane, but in this case, there is a presence of a mixture of inhibitors (methanol and sodium chloride). The fact that the produced water contains some quantities of salts, mostly sodium chloride, makes the study of gas hydrate dissociation conditions in the presence of aqueous solutions containing salts and alcohols/or glycols extremely important.

Table 4. Hydrate formation conditions for a mixture of methane, carbon dioxide and propane in the presence of methanol and sodium chloride.

T (K)	$x_{Methane}$	x_{CO_2}	$x_{Propane}$	$x_{Methanol}$ **(wt%)**	x_{NaCl} **(wt%)**	P_{exp} **(MPa)**	P_{Model} **(MPa)**	P_{CSMgem} **(MPa)**	AAD_{Model}	AAD_{CSMGem}
285.65	0.794	0.187	0.019	0.0500	0.0500	8.490	10.284	9.094	21.13	7.110
283.13	0.802	0.178	0.020	0.0500	0.0500	5.961	6.356	5.819	6.630	2.370
277.50	0.82	0.160	0.020	0.0500	0.0500	2.672	2.978	2.582	11.44	3.350
280.09	0.794	0.187	0.019	0.1001	0.0999	9.744	8.865	7.376	9.020	24.30
277.30	0.804	0.177	0.019	0.1001	0.0999	5.767	5.469	4.666	5.170	19.08
274.78	0.821	0.159	0.020	0.1001	0.0999	3.853	3.734	3.195	3.080	17.08
279.66	0.810	0.172	0.018	0.1000	0.1000	8.590	9.408	6.916	9.530	19.49
278.90	0.807	0.175	0.018	0.1000	0.1000	8.161	8.223	6.104	0.760	25.20
279.88	0.805	0.177	0.018	0.1000	0.1000	9.452	10.569	7.226	11.82	23.55
279.96	0.798	0.183	0.019	0.1497	0.0498	8.250	7.001	6.793	15.14	17.66
277.50	0.804	0.176	0.020	0.1497	0.0498	5.632	4.701	4.500	16.52	20.09
273.81	0.824	0.156	0.020	0.1497	0.0498	3.443	2.884	2.714	16.24	21.18
									10.54	16.71

Source: Experimental data from Bishnoi and Dholabhai (1999).

5. CONCLUSION

In this work, a multiphase flash calculation was developed and implemented in Fortran90 to predict hydrate formation conditions (pressure and temperature). The systems that were analyzed included complex multicomponent mixtures (hydrocarbons, carbon dioxide, nitrogen), including the presence of thermodynamic inhibitors mixtures (salts, alcohols and glycols). The model used for modeling the hydrate phase was proposed by van der Waals and Platteeuw (1959), the other phases present in the system were modeled by the Cubic-Plus-Association (CPA) state equation.

In general, the results obtained were satisfactory, presenting a good agreement with the experimental data available in the literature for the several analyzed systems. The performance of the developed model was similar in relation to the CSMGem, the latter being a reference program in the phase equilibria modelling with the presence of hydrates. It can be seen that the model performed significantly better in regions of high pressures, salt-inhibited systems and in complex multicomponent systems in the presence of mixtures of inhibitors.

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