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AN INVESTIGATION OF THE PREDICTION OF HYDRATE FORMATION CONDITIONS IN THE PRESENCE OF THERMODYNAMIC INHIBITORS

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Abstract. *Gas hydrates are crystalline compounds, solid inclusion bodies of hydrogen bonded water and small guest molecules, typically light gases. They are notorious for causing problems for producers and processors in the oil and gas industry. Gas hydrates can form at pressures and temperatures found in natural gas and oil production pipelines causing blockages. In order to inhibit the formation of hydrates, the industry injects chemicals, such as alcohols (ethanol, methanol, mono-ethylene glycol, etc) and salts (sodium, magnesium and potassium chloride). The purpose of this work is to briefly review the literature for hydrate formation in mixtures containing light gases (hydrocarbons and carbon dioxide) and water in the presence of thermodynamic inhibitors. Four calculation methods to predict hydrate formation for these systems were examined and compared. Three commercial packages, Multiflash, PVTSim and CSMGem, and a hydrate prediction routine in Fortran, that used the van der Waals and Platteeuw theory and Peng-Robinson equation of state, were tested. Predictions of the four methods have been compared against independent experimental data from the open literature. In general the four methods were found to be reasonably in the predictions of experimental data. CSMGem and Multiflash showed the best results.*

Keywords: *Hydrates, Inhibitor, Prediction, Commercial Packages, Hydrate Routine*

1. INTRODUCTION

Gas hydrates are ice-like crystalline molecular complexes which are constituted of two groups of components: host and guest molecules. The host molecules is water, which forms structures via hydrogen bonding interactions to enclose guest molecules under suitable pressure and temperature conditions (Sloan and Koh, 2008). Hydrates are one of the main problems faced by the oil and gas industry, as once formed, they can agglomerate and produce plugs that interrupt flow in the flowlines. This can occur in gas, gas/condensate, and oil production lines.

In most offshore operations, hydrate formation is controlled by injection of a thermodynamic hydrate inhibitor, such as alcohols (ethanol, methanol, mono-ethylene glycol, etc.). The prevention of hydrate formation and safe removal of hydrate plugs represent high costs and safety concerns in deepwater flow assurance challenges.

Among the common gases produced in the petroleum industry, methane, ethane, isobutane, propane, nitrogen, hydrogen sulfide and carbon dioxide are all hydrate formers (Carroll, 2004). It is well-know that carbon dioxide (CO_2) is one of the most common non-hydrocarbon gas found in petroleum reservoirs. In addition, most of the Pre-Salt fields in Brazil hold a significant amount of CO_2, as high as 80% (Jahn *et al.*, 2012). The pressure and temperature conditions in deepwater petroleum production (as that found in Pre-Salt fields) are very propitious to hydrate formation. Thus, experimental and simulations studies of hydrates, especially with high carbon dioxide content, are important to oil and gas industry.

Knowing and understanding the pressure and temperature conditions conducive to gas hydrate formation is one of the first step in controlling hydrate formation. A number of simulators can predict the pressure/temperature conditions for hydrate formation. The thermodynamic models used in these simulators usually differ, especially in the calculation of the chemical potential of the aqueous phase, the effect of higher-molecular-weight hydrocarbons, the impact of hydrate inhibitors, and the equation of state to obtain the fugacities of each component in each phase. A full understanding of the models used in the available simulators is needed to assess the quality of the predictions for hydrate formation.

Only a few studies in literature have done a comparative assessment of models/simulators for hydrate prediction.

Carroll (2004) examined and compared seven methods for predicting hydrate formation in mixtures containing hydrogen sulfide. For the set of data examined (almost 125 experimental points), the computer methods CSMHYD and Equi-Phase were reasonably accurate. The authors concluded that these two methods were able to predict that the hydrate formation temperature to within 1.7°C 90% of the time.

Ballard and Sloan (2004) compared the predictions from CSMGem, the hydrate program from the Colorado School of Mines, with CSMHYD (predecessor to CSMGem), and three commercial hydrate prediction programs (DBRHydrate, Multiflash, and PVTsim). The comparisons were broken into two categories for hydrate formation temperatures and pressures, uninhibited and thermodynamically inhibited systems. The authors concluded that all simulators compared favorably, giving results within about 1°C.

The objective of this work is to briefly review the literature for hydrate formation in mixtures containing carbon dioxide with other light hydrocarbons in the presence of thermodynamic inhibitors. Four simulators to predict hydrate formation for these systems will be examined and compared: two commercial programs (Multiflash, PVTsim), CSMGem, and a our own hydrate prediction program that uses the van der Waals and Platteeuw model (van der Waals and Platteeuw, 1959) coupled with the Peng-Robinson equation of state (EoS) (Peng and Robinson, 1976).

2. CALCULATION METHODS

The objective of this study is to compare the hydrate prediction programs for the hydrate formation pressure for inhibited and uninhibited systems, focusing mainly in systems containing carbon dioxide. The comparisons are divided into two categories for hydrate formation pressure: (1) uninhibited systems, and (2) thermodynamically inhibited systems. These two categories are divided into two subcategories: single/simple hydrate (only one guest) and more than one guest or mixture of gases.

Four simulators for predicting hydrate formation are considered:

1. CSMGem from the Colorado School of Mines (version 1.10, release date January 1, 2007)
2. Multiflash from Infochem/KBC Advanced Technologies (DLL version 4.4.13)
3. PVTsim from Calsep A/S (revision 1.2.40 flexlm version)
4. Hydrate model from NUEM/Federal Technological University of Parana

All first three simulators (CSMGem, Multiflash, and PVTsim) are based on rigorous thermodynamic models. They simulate hydrate formation conditions of gas and oil mixtures and can deal with the most commonly used hydrate thermodyanmic inhibitors (methanol, ethanol, glycols, and salts). If the aqueous phase contains salts, the influence of the salts on the hydrate formation conditions will also be taken into account. The programs calculate the equilibrium conditions, amounts and types of hydrates (structures I, II and H), and composition of the phases present (i.e., hydrocarbon, aqueous, and solids phases). Details of the hydrate model from NUEM/UTFPR is presented in the next subsection.

2.1 NUEM/UTFPR Hydrate Model

Kakitani (2014) implemented a model to predict the hydrate equilibrium formation. The basic assumption of the model concerns the chemical potential of water. At equlibrium, the chemical potential must be equal in all phases present, e.g.,

$$\mu_w^H = \mu_w^L = \mu_w^V \tag{1}$$

where superscripts H stands for hydrate phase, L for liquid phase, V for vapor phase, and the subscript w for water.

The water chemical potential in the liquid phase is obtained from classical thermodynamic as

$$\mu_w^L = \mu_w^0 + RTln\left(\frac{f_w^L}{f_w^0}\right) \tag{2}$$

where f is the fugacity and the superscript 0 stands for a reference state for water.

The water chemical potential in the hydrate phase was obtained from the statistical thermodynamic, more precisely from the van der Waals and Platteeuw (1959) model, as

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

where the superscript β stands for a hypothetical phase in a crystalline configuration of empty water cavities, v_i is the number of cavities type i per water molecule in the hydrate structure and Y_{ki} is the fractional occupancy of component k

in cavity type i. In this work, the water chemical potential in the vapor phase was not considered once was assumed that the solubility of water in vapor is negligible.

Substituting Eqs. (2) and (3) in Eq. (1), and applying the Gibbs-Duhem equation, the equation in terms of measurable variables (p, T) is

$$\frac{\Delta\mu_0}{RT_0} - \int_{T_0}^{T} \frac{(\Delta H_0 + \int_{T_0}^{T} C_p dT)}{RT^2} dT + \frac{\Delta V_0}{R\bar{T}} (p - p_0) = \ln\left(a_W^L\right) - \sum_i v_i ln\left(1 - \sum_k Y_{ki}\right) \tag{4}$$

where $\Delta\mu_0$, ΔH_0 and ΔV_0 are the differences in chemical potentials, molar enthalpies and molar volumes, respectively, between water in empty cavities and the reference state. These are tabulated values (Kakitani, 2014; Sloan and Koh, 2008).

Equation (4) is the expression that must be solved to obtain the state conditions for the hydrate equilibrium formation for a specific gas (guest). It is an implicit expression in pressure (p), so it is necessary an iterative process to calculate the equilibrium pressure for any temperature (T). This equation is implemented in a Fortran code and solved by the secant method.

Fugacities of the gaseous components are calculated by Peng and Robinson (1976) equation of state. Fugacities of water in the liquid phase are calculated from

$$\hat{a}_w = \frac{\hat{f}_w}{f_w^0} \tag{5}$$

From the definition of activity coefficient in a liquid mixture,

$$\gamma_w = \frac{\hat{a}_w}{x_w} \tag{6}$$

here, x_w is the mole fraction of free water available to form hydrates.

Thus, the water fugacity in a liquid mixture in the presence of an inhibitor is

$$\hat{f}_w = x_w \gamma_w f_w^0 \tag{7}$$

If there is no addition of inhibitors, the activity coefficient is unity and the water fugacity is proportional to the mole fraction of free water (x_w). It is also necessary to evaluate the effect of gas solubility in water ($x_g = 1 - x_w$). As the gas solubility increases in the liquid water, mole fraction of water decreases, thus decreasing the activity of water. Sloan and Koh (2008) proposed the use of Krichevsky and Kasaranovsky (1935) correlation to calculate the mole fraction of water. This correlation is used in this work.

The fractional occupancy of component k in the cavity type i, (Y_{ki}), is described by

$$Y_{ki} = \frac{C_{ki} f_k}{(1 + \sum_i C_{ji} f_i)} \tag{8}$$

where C_{ki} is the Langmuir constant for gas component k in cavity type i and f_k is the fugacity of component k in the vapor phase. Parrish and Prausnitz (1972) improved the van der Waals and Platteeuw (1959) and McKoy and Sinanoglu (1963) models. They used the following expression to calculate the Langmuir constants

$$C_{ki} = \frac{4\pi}{kT} \int_0^r exp\left(-\frac{\omega(r)}{kT}\right) r^2 dr \tag{9}$$

where $\omega(r)$ is the intermolecular potential between the guest and the host, k is the Boltzmann constant, and r is the radial position. Parrish and Prausnitz (1972) and McKoy and Sinanoglu (1963) used the Kihara potential to account for the intermolecular potential.

Munk *et al.* (1988) proposed the following expression to calculate the Langmuir constants

$$C_{ki} = \left(\frac{A_{ki}}{T}\right) exp\left(\frac{B_{ki}}{T}\right) \tag{10}$$

where A_{ki} and B_{ki} are tabulated values adjusted to experimental data. In this study, the Langmuir constants were calculated in two ways: using the expression proposed by Munk *et al.* (1988) (Eq. 10) and using the Kihara potential (Eq. 11) (McKoy and Sinanoglu, 1963).

For further details about the model and solution algorithm in the implementation, see Kakitani (2014).

Table 1. Experimental data used to compare the models.

System	Reference	Number of Points
$CO_2 + H_2O$	(Adisasmito *et al.*, 1991)	9
$CO_2 + H_2O$	(Fan and Guo, 1999)	9
$CO_2 + H_2O$	(Hachikubo *et al.*, 2002)	7
$CO_2 + H_2O$	(Ohgaki *et al.*, 1993)	7
$CO_2 + H_2O$	(Wendland *et al.*, 1999)	9
$CO_2 + H_2O$	(Ng and Robinson, 1983)	3
$CH_4 + H_2O$	(Jager and Sloan, 2001)	12
$CH_4 + H_2O$	(Svartas and Fadness, 1992)	7
$CH_4 + CO_2 + H_2O$	(Kakitani, 2014)	8
$CO_2 + N_2 + H_2O$	(Fan and Guo, 1999)	9
$CO_2 + H_2O + KCl$	(Dholabhai *et al.*, 1993)	21
$CO_2 + N_2 + H_2O + NaCl$	(Fan and Guo, 1999)	7
$CH_4 + H_2O + CH_4O$	(Svartas and Fadness, 1992)	39
$CH_4 + H_2O + NaCl$	(Kobayashi *et al.*, 1951)	15
$CH_4 + H_2O + C_2H_6O$	(Kobayashi *et al.*, 1951)	5
$CH_4 + CO_2 + H_2O + CH_4O$	(Ng and Robinson, 1983)	25
$CO_2 + H_2O + CH_4O$	(Ng and Robinson, 1983)	13
$CO_2 + H_2O + C_2H_6O$	(Fan *et al.*, 2000)	4
$C_2H_6 + H_2O + KCl + CaCl_2$	(Englezos and Bishnoi, 1991)	5

2.2 Data Analysis

Predictions from the four methods have been compared against independent experimental data from the open literature. Table 1 shows the systems and citing literature. In this study, a total of 214 experimental points are examined.

The four methods discussed above were used to calculate the hydrate equilibrium pressure, at a fixed temperature, point-by-point and the results are presented as average absolute deviation, AAD,

$$AAD = \frac{100}{n}\sum_{i=1}^{n}\left|\frac{p_i^{exp} - p_i^{cal}}{p_i^{exp}}\right| \tag{11}$$

where n is the number of points, p_i^{exp} is the experimental pressure and p_i^{cal} is the calculated pressure for point i.

3. RESULTS AND DISCUSSION

Each of the calculation methods discussed above was used to estimate the hydrate equilibrium pressure for each of the data sets. Figure 1 shows the $AADs$ of each calculation method for uninhibited systems. Figure 1(a) is for single guest and Figure 1(b) is for more than one guest. Figure 1(a) and 1(b) suggest that one can expect the incipient hydrate pressure to be predicted to within 11% and 8% of pressure, for single guest and for more than one guest, respectively. However, from Fig. 1(b), it is apparent that more reliable thermodynamic data are needed for more than one guest systems. The $AADs$ for both CSMGem and Multiflash are about 2% and 3% for single guest, respectively, and 3% and 3.5% for more than one guest systems, respectively. It can be observed that the NUEM-UTFPR model that uses the Munk correlation (Munk *et al.*, 1988) was better for systems with single guest. Nevertheles, this behaviour did not repeat for systems with more than one guest.

Figure 2 is a parity plot for the various prediction methods using uninhibited hydrate data. This graph is a plot of the predicted pressure as a function of experimental hydrate equilibrium pressure. If the prediction method were a perfect fit of the experimental data then all of the points would lie on the $x = y$ line. Also plotted on the graph are error bands that deviates from the experimental pressure by $\pm 10\%$. In general, this parity plot do not reveal much more than the error graphs presented earlier. However, the plot demonstrated that these methods tend to under-predict the hydrate equilibrium pressure, with the exception of the Fortran's routine using the Kihara potential. On this plot the majority of the points are below the $x = y$ line. I also can be observed that the inaccuracies in the three commercial packages tend to be inside the error bard of $\pm 10\%$ even in at higher pressures.

Figure 3 compares the prediction for system containing thermodynamic inhibitors for single guest hydrate. Figure 3(a) and 3(b) are for inhibited systems with salts and alcohols, respectively. As expected, the $AADs$ for the inhibited systems are larger than for uninhibited for all calculation methods. From these figures, one can expect commercial packages to predict the salt- and alcohol-inhibited incipient pressure to within about 9%. While comparisons for the NUEM-UTPFR

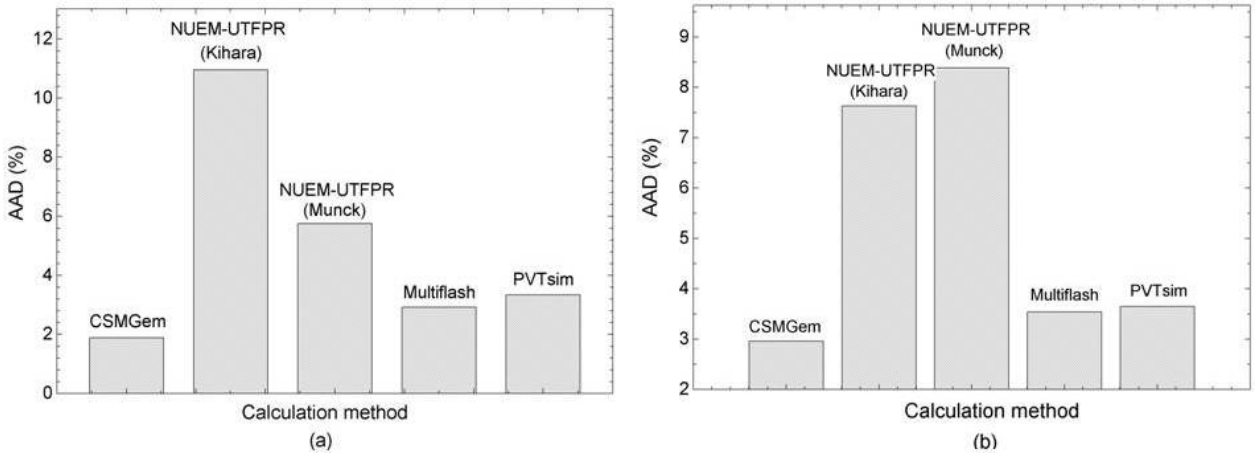

Figure 1. Incipient pressure accuracy for uninhibited hydrate data. (a) Single guest (63 points). (b) More than one guest (17 points)

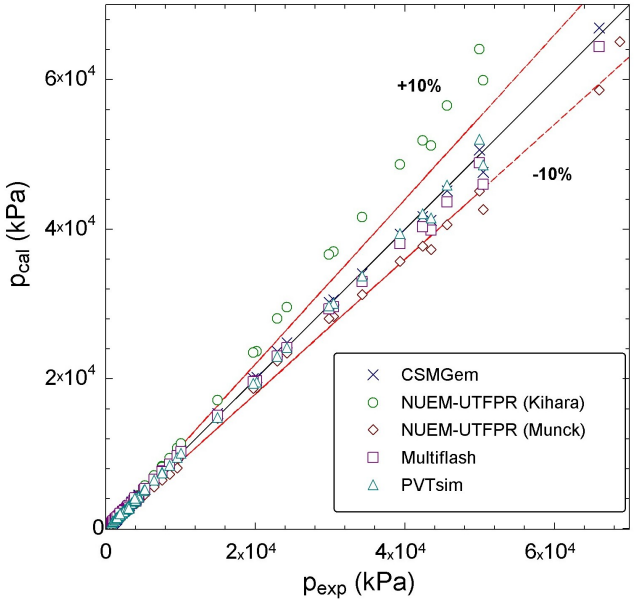

Figure 2. Comparison of predictions using uninhibited hydrate equilibrium data (total of 80 points).

model for the incipient pressure are within about 19%. For the inhibited systems the model using Munk's correlation was slightly better than Kihara potential.

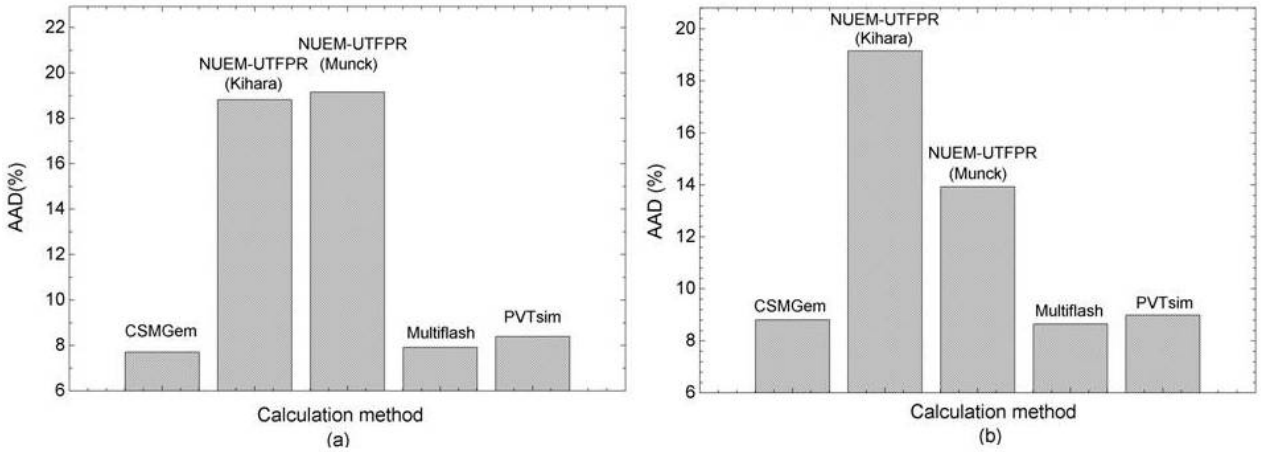

Figure 3. Incipient pressure for inhibited single guest hydrate data with (a) Salts (43 points) and (b) Alcohols (86 points).

Figure 4 is the incipient pressure for inhibited hydrate data for more than one guest systems. One may expect commercial packages to predict inhibited incipient pressure to within about 10%. Multiflash shows the best results. This figure also shows that the inaccuracies of mixtures of gases are higher than single guest in inhibited systems. For the NUEM-UTPFR model, the incipient pressure are predicted within about 20%. Once again the model using Munk's correlation was slightly better than Kihara potential.

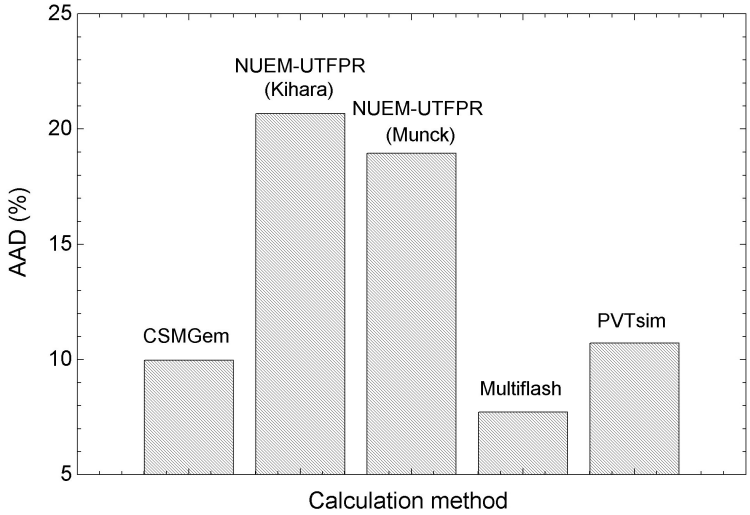

Figure 4. Incipient pressure for inhibited hydrate data (more than one guest hydrate data - 32 points).

Figure 5 shows the parity plot for the predictions for the inhibited hydrate equilibrium data. The plot shows that the models considered tend to over-predict the hydrate equilibrium pressure, with the exception of the NUEM-UTFPR model using the Munk's correlation. The inaccuracies in the three commercial packages tend to be inside the error bounds of $\pm 10\%$ even at higher pressures. The NUEM-UTFPR model using the Kihara potential fails for pressures above 20,000 kPa.

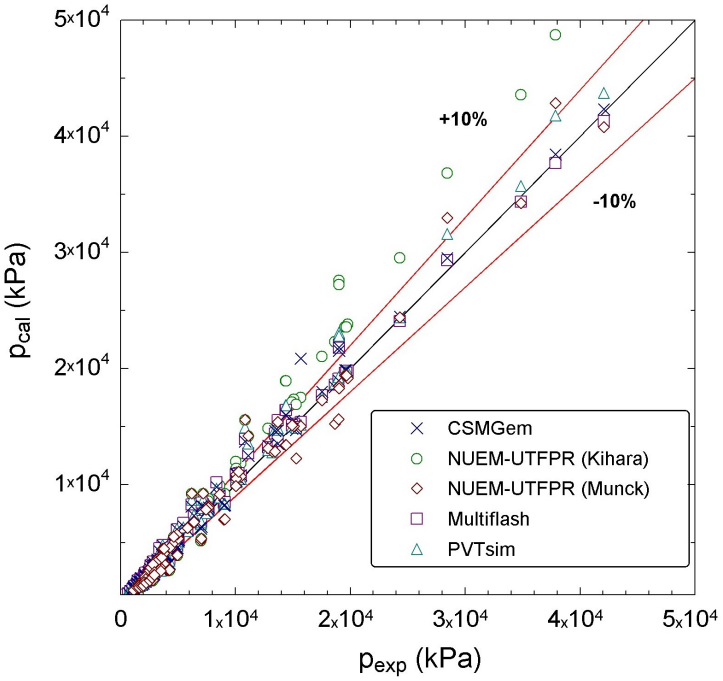

Figure 5. Parity plot for the predictions using inhibited hydrate equilibrium data (134 points).

In conclusion, Figure 6 presents the incipient pressure accuracy for all hydrate equilibrium data considered. It can be observed that the $AADs$ are 6.1%, 15.3%, 11.8%, 6.3% and 6.9% for CSMGem, NUEM-UTFPR model with Kihara, NUEM-UTFPR model with Munk, Multiflash, and PVTsim, respectively. The results for CSMGem and Multiflash are very simlar, but CSMGem was somewhat superior.

In a general, CSMGem proved to show the best results for uninhibited systems, followed by Multiflash and PVTsim.

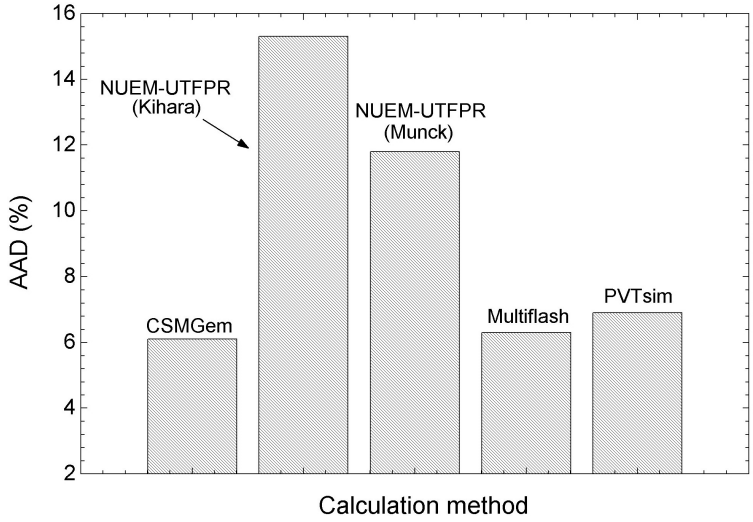

Figure 6. Incipient pressure accuracy for all hydrate equilibrium data (214 points).

However, for inhibited systems the AAD of the three commercial packages are very similar in one guest systems and Multiflash demonstrated to work better with more than one guest systems. The NUEM-UTFPR model showed to be less accurate than the three commercial softwares evaluated.

It can be added that all models used the van der Waals and Platteeuw (1959) model for the hydrate phase. However, the fluid phase are treated by different equations of state. CSMGem uses the Soave-Redlich-Kwong (SRK) Eos, Multiflash uses the Cubic-Plus-Association (CPA) EoS, and PVTsim uses the Peng-Robinson (PR) EoS. This information together with the type of activity coefficient equation used in the models could assist in understanding the differences between the calculations methods. Unfortunately, the commercial packages are not explicit in the activity coefficient models considered. Certain activity coefficient models are more adequate to deal with specific inhibitors like salts or alcohols. Concerning the equations of state, it is well know that cubic EoS are more conservative and general, despite the good results for hydrocarbon fluids phase equilibria. The CPA EoS combines the classical simple SRK equation with an association term (Kontogeorgis *et al.*, 1996). Thus, the EoS has a "physical" part from the cubic EoS and a "chemical" part from the Associations Theory. CPA has attracted the interest of the oil and gas industry, not just because of successful simulations over extended temperature and pressure ranges, but also because of the capability of the model to predict multicomponent, multiphase equilibria. In hydrate models, CPA represents successfully the partitioning of inhibitor between vapor and aqueous phases.

The NUEM-UTFPR model to predict hydrate equilibrium formation presented the largest deviations. However, for engineering purpose, it could be an initial tool for estimating hydrate equilibrium predictions. This model is the first step in a series of improvements, including a flash calculation using CPA EoS to consider the gas solubility in the aqueous phase and the water solubility in the vapor phase, as well as inhibitor partitioning between vapor and aqueous phases.

4. CONCLUSIONS

After reviewing available carbon dioxide hydrate equilibrium data in the literature, four calculation methods to predict hydrate formation were examined and compared. The results presented here do not represent conclusive proof, but they provide some evidence for using the calculation methods chosen.

The investigated methods for predicting hydrate conditions are reasonably accurate for the evaluated systems. The total absolute average deviation in the predicted hydrate pressure are: 6.1%, 15.3%, 11.8%, 6.3% and 6.9% for CSMGem, Multiflash, PVTSim, NUEM-UTFPR model with Kihara potential, and NUEM-UTFPR model with Munk correlation, respectively. Therefore, CSMGem shows the best results for uninhibited systems, followed by Multiflash and PVTsim. For inhibited systems the deviations of the three commercial packages are very similar in one guest systems, and Multiflash demonstrate to work better with gas mixtures.

The NUEM-UTFPR model presented the largest deviations among the four calculation methods evaluated. The results using Munk correlation were better than using Kihara potential. This model is being improved and will be further refined in the future.

Based on this study, we can also conclude that there is a scarcity of carbon dioxide hydrate equilibrium data to make a complete comparison between the calculation methods.

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6. REFERENCES

Adisasmito, S., Frank, R.J. and Sloan, E.D., 1991. "Hydrates of carbon dioxide and methane mixtures". *Journal of Chemical Engineering Data ,*, Vol. 36(1), pp. 68–71.

Ballard, A.L. and Sloan, E.D., 2004. "The next generation of hydrate prediction IV: A comparison of available hydrate prediction programs". *Fluid Phase Equilibria*, Vol. 216, pp. 257–270.

Carroll, J.J., 2004. "An examination of the prediction of hydrate formation conditions in sour natural gas". In *GPA Europe, Spring Meeting*.

Dholabhai, P.D., Kalogerakis, N. and Bishnoi, P.R., 1993. "Equilibrium conditions for carbon dioxide hydrate formation in aqueous electrolyte solutions". *Journal of Chemicla Enginering Data*, Vol. 38, pp. 650–654.

Englezos, P. and Bishnoi, P.R., 1991. "Experimental study on the equilibrium ethane hydrate formation conditions in aqueous electrolyte solutions". *Industrial Engineering Chemical Research*, Vol. 30, pp. 1655–1659.

Fan, S. and Guo, T.M., 1999. "Hydrate formation of CO_2-rich binary and quaternary gas mixtures in aqueous sodium chloride solutions". *Journal of theAmerican Chemical Society*, Vol. 44, pp. 829–832.

Fan, S.S., Chen, G.J., Ma, Q.L. and Guo, T.M., 2000. "Experimental and modeling studies on the hydrate formation of CO_2 and CO_2-rich gas mixtures". *Chemical Engineering Journal*, Vol. 78, pp. 173–178.

Hachikubo, A., Miyamoto, A., Hyakutake, K., Abe, K. and Shoji, H., 2002. "Phase equilibrium studies on gas hydrates formed from various guest molecules and powder ice". In *The Fourth International Conference on Gas Hydrates, Yokohama, Japan, 19-23, pp 357-360*.

Jager, M.D. and Sloan, E.D., 2001. "The effect of pressure on methane hydration in pure water and sodium chloride solutions". *Fluid Phase Equilibria*, Vol. 185, pp. 89–99.

Jahn, F., Cook, M., Graham, M. and Ferreira, D., 2012. *Hydrocarbon Exploration and Production*. Elsevier.

Kakitani, C., 2014. *Estudo do equilíbrio de fases de hidratos de metano e da mistura metano e dióxido de carbono*. Master's thesis, PPGEM-Universidade Tecnológica Federal do Paraná.

Kobayashi, R., Withrow, H.J., Williams, B. and Katz, D.L., 1951. "Gas hydrate formation with brine and ethanol solutions". In *30th Annual Convention Natural gasoline Association of America, pp 27-31*.

Kontogeorgis, G.M., Voutsas, E.C., Yakoumis, I.V. and Tassios, D.P., 1996. "An equation of state for assciating fluids". *Industrial Engineering Chemical Research*, Vol. 35, pp. 4310–4318.

Krichevsky, I.R. and Kasaranovsky, J.S., 1935. "Thermodynamical calculations of solubilities of nitrogen and hydrogen in water at high pressures". *Journal of American Chemical Society*, Vol. 57, pp. 2168–2171.

McKoy, V. and Sinanoglu, O., 1963. "Theory of dissociations pressures of some gas hydrates". *Journal of Chemical Physics*, Vol. 38, p. 2946.

Munk, J., Skjold-Jorgensen, S. and Rasmunssen, P., 1988. "Computations of the formation of gas hydrates". *Chemical Engineering Sciences*, Vol. 43, pp. 2661–2672.

Ng, H.J. and Robinson, D.B., 1983. "Equilibrium phase composition and hydrating conditions in systems containing methanol, light hydrocarbons, carbon dioxide and hydrogen sulfide". In *Data Base*.

Ohgaki, K., Makihara, Y. and Takano, K., 1993. "Formation of CO_2 hydrate in pure and sea waters". *Jounal of Chemical Engineering of Japan*, Vol. 26(5), pp. 558–564.

Parrish, W.R. and Prausnitz, J.M., 1972. "Dissociation pressures of gas hydrates formed by gas mixtures". *Industrial & Engineering Chemistry Process Design and Development*, Vol. 11(1), pp. 26–35.

Peng, D.Y. and Robinson, D.B., 1976. "A new two-constant equation of state". *ndustrial and Engineering Chemistry: Fundamentals*, Vol. 15, p. 59Ű64.

Sloan, E.D. and Koh, C.A., 2008. *Clathrate Hydrates of Natural Gases*. CRC Press/Taylor & Francis.

Svartas, T.M. and Fadness, F.H., 1992. "Methane hydrate equilibrium data for the methane-water-methanol system up to 500 bara". In *Second International Offshore and Polar Engineering Conference, San Francisco , June 14-19, pp 614-619*.

van der Waals, J.H. and Platteeuw, J.C., 1959. "Clathrate solutions". *Advances in Chemical Physics*, Vol. 2(21), pp. 1–55.

Wendland, M., Hasse, H. and Maurer, G., 1999. "Experimental pressure-temperature data on three- and four-phase equililbria of fluid, hydrate, and ice phases in the system carbon dioxide-water". *J. Chem. Eng. Data*, Vol. 44, pp. 901–906.

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