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Modelling of methane gas hydrate incipient conditions via translated Trebble-Bishnoi-Salim equation of state

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Gas hydrates are crystalline inclusions of water and gas that form when an aqueous phase is contacted with low molecular weight gases such as the light hydrocarbons, at appropriate conditions of temperatures and pressures. Gas hydrates are of interest to gas industry not only because they tend to plug gas and oil pipelines but also because they are potentially considered as important future fuel energy. Historically, predictions of gas hydrate equilibrium conditions have been made using the statistical model of Van der Waals and Plaateeuw, to describe the solid phase, and equation of state to describe the vapour phase. Recently, the Trebble-Bishnoi-Salim equation of state was extended to the solid phase to predict CO_2 freeze out conditions in natural gases. In this work, the translated Trebble-Bishnoi-Salim equation of state is applied to methane hydrates. Binary interaction parameter (Ka) for water and hydrated-methane was regressed from experimental data and the model was then used to predict the hydrate-water-vapour three-phase equilibrium conditions over a wide range of temperature. The predictions were found to closely match the experimental data and the use of a single equation of state for the solid, liquid and vapour phase was shown to be an efficient alternative to the traditional method.

1. INTRODUCTION

Gas clathrates (commonly called gas hydrates) are a group of nonstoichimetric, ice-like crystalline solids made up of combination of water and suitable sized guest molecules under conditions of high pressure and low temperature. In these systems water molecules form a hydrogen-bonded lattice with large interstitial cavities, which generally encage small gas molecules such as methane, ethane, propane, carbon dioxide, nitrogen etc.

Although studies have historically focus on gas hydrates as troublemakers, due to the plugging of natural gas pipelines and interfering with natural gas processing and transportation, gas hydrates have also a potential application for commercial applications such as: potential energy source due to their outstanding capacity to store large amount of gas (Ginsburg and Soloviev, 1995), a mean to sequestrate carbon dioxide allowing to reduce the amount of greenhouse gases in the atmosphere (Brewer et al., 1999), a safe storage, transportation and production of natural gas (Gudmundsson

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and Borrehaug, 1996) ; as mean for in-situ control of the droplet size in reverse micellar systems which can be used to manipulate some of the properties of the materials that have been formed in the water droplet (Nguyen et al., 1993).

Traditionally, predictions of gas hydrate equilibrium conditions have been made using the statistical thermodynamic model of van der Waals and Plaateeuw (1959) who presented the hydrate formation as adsorption-type process. The result of this analysis provides an expression for the chemical potential difference of the filled hydrate lattice and the hypothetical empty hydrate lattice. Based on that, Parrish and Prautnitz (1972) developed an algorithm to calculate the dissociation curve of clathrate hydrates in pure water. This procedure has been broadly accepted for the generation of commercial software packages. Lately, equations of state have been used to describe the thermodynamic behaviour of solid, liquid and vapour phases (Wentzel and Smith, 1980; Salim and Trebble, 1994; Modarress et al, 1999; Yokozeki, 2003). In addition, Yokozeki (2005), extended the use of his equation of state to predict the phase behaviour of methane gas hydrates, obtaining good agreement with the experimental data. In this work, the translated Trebble-Bishoi-Salim equation of state is used as an alternative method to predict the univariant three phase (gas + liquid water/ice + hydrate) equilibrium line for the two component (water and gas) system. Under this scheme, methane hydrates are treated as impure solids, thus the binary interaction parameter for water and hydrated-methane was regressed from experimental data and then the model was then used to predict the hydrate-water-vapour three-phase equilibrium conditions over a wide range of temperature.

2. THERMODYNAMIC MODEL

Salim and Trebble (1994) demonstrated a methodology by which a cubic equation of state can be modified to allow the calculation of equilibrium conditions involving solid phases as well as thermodynamic properties of the solid phase itself. The procedure consists of the volume translation of the Trebble-Bishnoi-Salim equation of state at the triple point, which is to be performed using experimental values of the solid density. In addition, temperature-dependent parameters are to be then regressed to vapour pressure data at temperatures below the triple point if data are available. Translation of the TBS Equation of State at the triple point (denoted by "-") results in the following form:

$$P = \frac{RT}{v-\bar{b}} - \frac{\bar{a}\hat{\alpha}}{v^2 + (\bar{b}+\bar{c})v - (\bar{b}\bar{c}+\bar{d}^2)} \tag{1}$$

Where

$$\hat{\alpha} = 1 + \hat{m}(\bar{T}_r - T_r) + \hat{p}(\bar{T}_r \ln \bar{T}_r - T_r \ln T_r) \tag{2}$$

$$\bar{T}_r = \bar{T}/T_c \tag{3}$$

The constants a, b, c and d were determined by Salim and Trebble imposing four conditions:

- The translated equation of state must match the solid density at the triple point.
- Saturation pressure calculated from the original EOS at the triple point must be match by the translated equation.
- Solid phase fugacity from the translated equation of state must match the vapour phase fugacity from the translated Equation of State at the triple point.
- Vapour phase fugacities calculated from both EOS and translated EOS must match at the triple point.

For methane hydrates components, the constants were reported by Salim and Trebble (1994) as shown in table 1:

Table 1 Parameters for the translated TBS EOS.

Components	m	p	a	b	c	d
Methane	8.67E-01	1.03E-01	3.14E-01	2.65E-05	3.03E-05	5.59E-06
Water	1.29E+00	2.61E-01	1.04E+00	1.83E-05	4.32E-05	1.30E-05

Subsequently, the original and translated TBS equations of state were incorporated in a pressure-temperature three-phase flash calculation. For this purpose, Nelson's algorithm (1987) was chosen due to its simplicity and reliability as method to work with.

Once, the Pressure-Temperature three-phase flash calculation is coupled with the equations of states, the binary interaction parameter for methane and water in hydrated phase was regressed in order to match the experimental composition of the gas hydrates on the equilibrium curve.

3. RESULTS AND DISCUSSION

In the present model a single binary interaction parameter (Ka) for the solid phase is used to represent the equilibrium conditions of the methane hydrates. The determination of this parameter was made using the data reported by Circone et al. (2005) who experimentally measured the composition of methane hydrates along the equilibrium curve, determining that the average value is $CH_4{\cdot}5.99(\pm0.07)H_2O$; where the pressure and temperature conditions ranged between from 1.9 to 9.7MPa and 263 to 285K. Considering this datum, the binary interaction parameter (Ka) for methane and water was estimated along the equilibrium curve (Adisasmito et al., 1991), as shown in table 2.

Table 2 Binary interaction parameter for methane hydrates using the translated TBS EOS.

Ka	Pressure (Pa)	Temperature (K)
-3.552	2680000	273.4
-3.731	3050000	274.6
-4.118	3720000	276.7
-4.482	4390000	278.3
-5.266	5770000	279.6
-5.895	6650000	280.9
-6.725	7590000	283.6

Based on these results, it is suitable for the purpose of computational calculations to correlate the binary interaction parameter (Ka) as function of the temperature through a polynomial function

$$Ka = -1.633*10^{-5}T^{5} + 2.245*10^{-2}T^{4} - 1.235*10T^{3} + 3.396*10^{3}T^{2} - 4.669*10^{5}T + 2.658*10^{7}$$

where T is kelvin (4)

Once incorporated this expression into the translated TBS equation of state, it is possible to predict the incipient conditions for methane hydrate formation with a good accuracy (maximum relative error 0.7%). Figure 1 compares the predictions with the experimental data reported by Adisasmito et al. (1991).

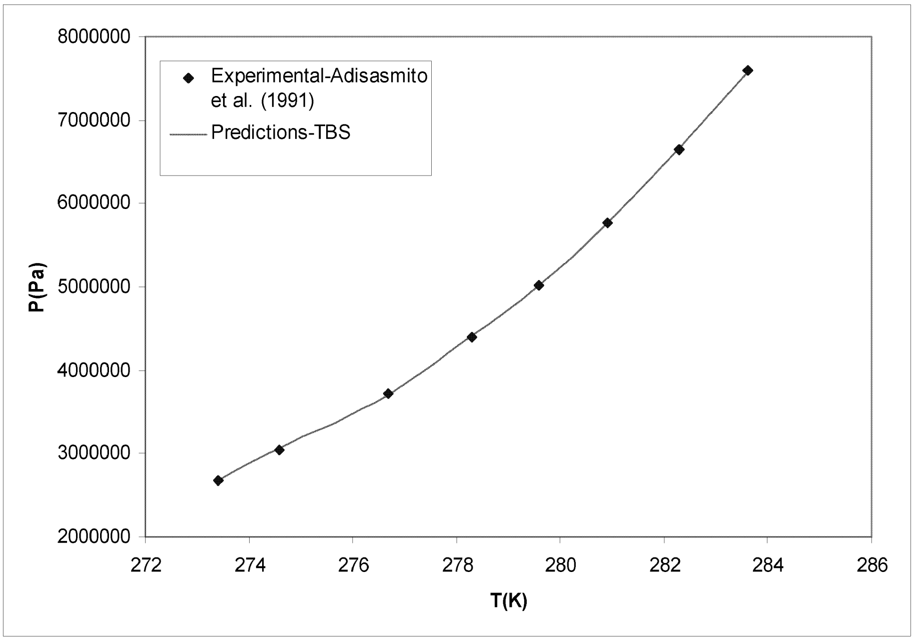

Figure 1. Methane hydrate equilibrium curve

Some of the main advantages of this approach with respect the one published by Yokozeki (2005), is the fact that in his model, two binary interaction parameters are required for the solid phase (hydrates). In addition, it is necessary to include a modifying factor (c_b) in the attractive interaction term (parameter b) of his equation of state. These facts allow that the predictions based on the original and the translated TBS equations of states are simpler and with a good degree of accuracy in the predictions of the incipient conditions.

4. CONCLUSIONS

Translated TBS equation of state demonstrated to be a useful tool to represent the hydrate solid phase.By combining the original equation and the translated one, it was possible to predict the incipient conditions for methane hydrate with good agreement with the experimental data, , requiring only a single binary interaction parameter (Ka). Using the same methodology presented above, it is possible that this scheme of calculation can be extended to other different components such as ethane, propane, n-butane etc.

5. REFERENCES

Adisasmito S., Frank R., and Sloan E.D., 1991, Hydrates of carbon dioxide and methane mixtures, J. chem. eng. data, 36, 68-71.

Brewer P.G., Friederich C., Peltzer E.T. and Orr F.M., 1999, Direct experiments on the ocean disposal of fossil fuel CO2, Science, 284 (5416), 943-925.

Circone S., Kirby S., Stern L., 2005, Direct measurement of methane hydrate composition along the hydrate equilibrium boundary, J. phys chem. B, 109, 9468-9475.

Ginsburg G.D. and Soloviev V.A., 1995, Submarine gas hydrate estimation: Theoretical and empirical approaches, 27th Offshore Technology Conference, Houston, Texas, 513-518.

Gundmundsson J. and Borrehaug A., 1996, Frozen hydrate for transport of natural gas, Proc. 2nd Int. Conference on Natural Gas Hydrates, 415-422.

Modarress E., Ahmadnia G. and Mansoori G., 1999, Improvement on Lennard-Jones-Davonshire theory for predicting liquid-solid phase transition, J. Chem Phys., 111, 10236-10241.

Nelson P.A., 1987, Rapid phase determination in multiphase flash calculations, Comput. Chem. Engng., 11(6), 581-591.

Nguyen H.T., Kommareddi N. and John V.T., 1989, Clathrate formation in reversed micellar solutions, Journal of Physical Chemistry, 93(25), 8213-8126.

Parrish W. and Prausnitz J., 1972 , Dissociation pressures of gas hydrates formed by gas mixtures, Ind. Engng. Chem. Process. Des. Dev. 11, 26-35

Salim P. and Trebble M., 1994, Modelling of solid phases in thermodynamic calculations via translation of a cubic equation of state at the triple point, Fluid Phase Equilibria, 93, 75-99.

Van der Waals J.H. and Platteeuw J.C., 1959, Clathrate solutions, Adv. Chem Phys., 2(1), 1-57.

Wentzel H. and Schmidt G., 1980, A modified van der Waals equation of state for the representation of phase equilibria between solids, liquid and gases, Fluid Phase Equilibria, 5, 3-17.

Yokozeki A., 2003, Analytical equation of state for solid-liquid-vapour phases, International journal of thermophysics, 24(3), 589-620

Yokozeki A., 2005, Methane gas hydrates viewed through unified solid-liquid-vapour equation of state, International journal of thermophysics, 26(3), 743-765.