Statistical thermodynamics model and empirical correlations for predicting mixed hydrate phase equilibria

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ABSTRACT

Natural gas hydrate deposits contain CH_4 along with other hydrocarbon gases like C_2H_6, C_3H_8 and non-hydrocarbon gases like CO_2 and H_2S. If CH_4 stored in natural gas hydrates can be recovered, the hydrates would potentially become a cleaner energy resource for the future producing less CO_2 when combusted than does coal. The production of CH_4 from natural gas hydrate reservoirs has been predicted by reservoir simulators that implement phase equilibrium data in order to predict various production scenarios. In this paper two methods are discussed for calculating the phase equilibria of mixed hydrates.

In the first method, the phase equilibrium is predicted using a 'cell potential' code, which is based on van der Waals and Platteeuw statistical mechanics, along with variable reference parameters to account for lattice distortion, and with temperature-dependent Langmuir constants proposed by Bazant and Trout. The method is validated by reproducing the existing phase equilibrium data of simple and mixed hydrates and the structural transitions that are known to occur, without the use of any fitting parameters. A computationally-simple method is to use empirical correlations of gas hydrate dissociation pressure with respect to temperature and gas-phase composition as they are easy to implement into the simulators. The parameters for the empirical expression were determined for the CH_4–C_2H_6 mixed hydrate system by non-linear regression analysis of available experimental data and data obtained from the first method.

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1. Introduction

Natural gas hydrates are crystalline non-stoichiometric compounds of water and gas that can be formed either: (i) from gas produced by bacterial activity at shallow depths which contains CH_4 with trace amounts of C_2H_6, or (ii) by thermal pyrolysis of fossil organic matter containing CH_4 and a significant amount of higher hydrocarbons (C_2–C_5) and non-hydrocarbon gases like CO_2 [1]. They are considered to contain more carbon than in all other fossil fuels reserves combined worldwide. Thus, if CH_4 stored in the natural gas hydrates can be recovered, the hydrates can become a valuable energy resource [2]. Reservoir simulators can be used to predict production potentials of hydrate wells. Reservoir simulators involve solutions of highly-complex combinations of fluid, heat

and mass transport equations and formation/dissociation of multiple solid phases. In the prediction of CH_4 production from hydrate reservoirs, the pressure and temperature of the I–H–V and L_w–H–V three-phase lines are of particular interest as they describe the limits of hydrate formation and dissociation conditions The regression equations used in current reservoir simulators for phase equilibrium predictions can be used only for pure CH_4 hydrates and they cannot predict the occupancies and composition of the hydrates. But, natural gas hydrates are not pure gas hydrates, as they contain trace amounts of other hydrocarbons and non-hydrocarbon gases along with methane. The CH_4 trapped in hydrate reservoirs can be recovered by injection of pure CO_2 and $CO_2 + N_2$; after replacing CH_4 from the natural gas hydrate they form mixed hydrate of CH_4–CO_2 and CH_4–CO_2–N_2 respectively. The phase equilibria and structure of the pure hydrate change significantly due to the addition of other guest components [1]. Hence, a computationally-tractable method has to be developed to implement into the existing reservoir models for mixed hydrates; this method should also be able to predict other hydrate properties.

There are various techniques used to determine the phase equilibria of the gas hydrates, e.g. the gas gravity method [3], the
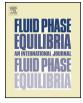
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K_{vsi} method [4], and statistical thermodynamic approaches. The gas gravity and K_{vsi} methods preceded the knowledge of the existence of different hydrate structures. Though they are simple and fast, they are not accurate and cannot be used for predictions involving different structures [1].

Recently, Bazant and Trout [5] proposed that a spherically-averaged intermolecular potential can be determined analytically by the temperature-dependent Langmuir constant. Starting from the statistical thermodynamic approach developed by van der Waals and Platteeuw [6] and incorporating the Lennard–Jones and Devonshire (LJD) approximation [7], cell potentials can be extracted directly from experimental equilibrium data by solving an integral equation analytically. In the van der Waals and Platteeuw [6] model, constant reference parameters for different guest molecules are assumed due to the assumption that there are no lattice distortions with the guest molecules. Later, Hwang et al. [8] found by molecular dynamic simulations on a unit cell of gas hydrates with different guest molecules that the guest molecules have an impact on the host–host interactions in the lattice; hence, the reference parameters should vary with the guest molecule.

In this study, a correlation is developed between the reference parameters and the guest molecule size by performing a linear regression analysis on experimentally determined values. The mixed hydrate reference parameters are calculated from the pure component reference parameters using mixing rules. Finally, the phase equilibria and structural transitions of the mixed hydrates can be predicted accurately without fitting to any experimental data. The model is validated by predicting the existing phase equilibria data of simple and mixed hydrates and the structural transitions that are known to occur. Though the method is computationally lengthy it could predict phase equilibria more accurately along with occupancies and composition of gas hydrates.

The full flash equilibrium calculation adds significant computational expense to a reservoir simulation; as these iterative flash calculations would be done at each iteration (2–8 times), for each timestep (1000 s of times), for every gridblock (1000–100,000). Therefore it is desirable to find computationally faster methods such as empirical correlations or to use lookup tables. A simple correlation is developed by empirically fitting different functional forms to available experimental data and data obtained from the cell potential code developed in the first method. The equilibrium pressure at a given temperature and gas composition for both structures is determined by the correlation which can be implemented into reservoir simulators easily. However, this method does not give information about the hydrate phase composition and occupancies.

2. Methods

The two methods that are used in this study for calculating the phase equilibria of gas hydrates are discussed in this section. The first method is using a cell potential code for variable chemical potential and enthalpy reference parameters for mixed hydrates, which is capable of predicting gas occupancies and composition in hydrate along with the phase equilibrium data. The second method discussed in Section 2.2 is to develop an empirical correlation for gas hydrate dissociation pressure with respect to temperature and gas composition; the parameters of the correlation are obtained by non-linear regression analysis.

2.1. Cell potential code for variable reference parameters

The cell potential code developed by Anderson et al. [9] is modified for variable reference parameters, and is based on the van der Waals and Platteeuw [6] statistical method, where the cage

occupancy θ_{Ji} is mathematically defined by the Langmuir adsorption isotherm and is related to the Langmuir constant as:

$$\theta_{Ji} = \frac{c_{Ji}f_J}{1 + \sum_J C_{Ji}f_J} \tag{1}$$

where f_J is the fugacity of guest molecule J calculated using the Peng–Robinson [10] equation of state and C_{Ji} is the Langmuir constant is given as

$$C_{Ji}(\beta) = 4\pi\beta \int_0^\infty e^{-\beta w(r)} r^2 dr \tag{2}$$

where $\beta = 1/kT$, k = Boltzmann constant and T = temperature (K).

In CSMGem [1] a Gibbs energy minimization method developed at Colorado School of Mines for calculating formation conditions of any phase, $w(r)$ is determined using experimentally-fitted Kihara parameters, the parameters are fitted to the hydrate-forming properties for each component [1], while in this model, Bazant and Trout's [5] method is used to obtain a functional form of the spherically-averaged intermolecular potential by analytically solving the equation for $w(r)$. In order to invert the equation for $w(r)$, a functional form of $C_{Ji}(\beta)$ is used. This is done by computing the values of the Langmuir constants from experimental dissociation data (for hydrates that have only large cages occupied) and ab initio potentials for hydrates that have both cages occupied. Using ab initio potentials Langmuir constants are calculated for methane and argon by Anderson et al. [9] and for carbon dioxide by Velaga and Anderson [11] for both structures. The computed Langmuir constants values are well fitted to van't Hoff temperature dependence given by

$$C_{Ji}(\beta) = C_{0Ji}e^{m_{Ji}\beta} \tag{3}$$

where C_0 and m are specific for each guest component J and cavity type i.

Holder et al. [12] proposed an equation for the chemical potential difference between water in an empty hydrate lattice and water in the liquid aqueous phase or in the ice phase as:

$$\frac{\Delta\mu_w^{\beta-L,\alpha}(T,P)}{kT} = \frac{\Delta\mu_w^0(T_0, 0)}{kT} - \int_{T_0}^T \left[\frac{\Delta h_w^0(T)}{kT^2}\right]_P dT$$
$$+ \int_0^P \left[\frac{\Delta V_w^{\beta-L,\alpha}}{kT}\right]_T dP - \ln\gamma_w x_w \tag{4}$$

In previous models, the reference parameters, and (J/mol) are taken to corresponding to the structure of the hydrate irrespective of the guest molecule. In this model, these values are calculated from the correlation developed with respect to the molecular diameters of the guest component [12], d_g (Å), by the regression analysis of the experimentally-calculated chemical potential and enthalpy reference parameters of CH_4 [13] and CO_2 [11] for structure I and Ar [13] and N_2 for structure II. The functional form of correlation is similar to the Lee and Holder [14] expression for the reference parameters with respect to Kihara [15] hard-core parameter a (pm).

for structure I:

$$\Delta\mu_w^0 = 1197.279\exp(0.0010933d_g)$$
$$\Delta h_w^0 = 1061.589\exp(0.022302d_g) \tag{5}$$

for structure II:

$$\Delta\mu_w^0 = 974.033\exp(0.02644d_g)$$
$$\Delta h_w^0 = 1044.658\exp(0.056329d_g) \tag{6}$$