Journal of Natural Gas Science and Engineering 14 (2013) 192–203

Contents lists available at SciVerse ScienceDirect

Journal of Natural Gas Science and Engineering

journal homepage: www.elsevier.com/locate/jngse

Effect of capillary term parameters on the thermodynamic modeling of methane hydrate formation in porous media

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ARTICLE INFO

Article history:
Received 6 July 2011
Received in revised form
10 February 2013
Accepted 14 June 2013
Available online 20 July 2013

Keywords:
Methane hydrates
Phase behavior
Wetting angle
Shape factor
Porous media

ABSTRACT

According to the solid-solution theory, the stability of gas hydrates is related to the activity of water. Geometrical constraints decrease the activity of water. Therefore, differences in phase behavior calculations of gas hydrates in porous media from gas hydrates in the bulk, stem from activity of water calculations. In this work, the effects of different parameters describing capillary forces on the results of methane-hydrate formation modeling are studied. Two different thermodynamic models are applied for calculations. The first model assumes a single-size porous media and the equality of chemical potential. The second model considers the pore size distribution and the equality of water fugacity as the equilibrium criteria. It is shown that the value of surface tension proposed by Uchida and co-workers yields the most accurate predictions compared to experimental results. In addition, values of shape factors (assuming a fixed wetting angle) are optimized using experimental data. The optimized values are correlated to the hydrate formation temperature. To validate the optimized shape–factor parameters, the correlated values are used for an additional set of experimental data, which leads to reduced errors. If the single-size pore modeling is used, percent of average absolute deviation (AAD%) decreases from 7.83% to 4.59% in L_W–H–V region and from 19.58% to 15.71% and 7.03% in the I–H–V region for perfect wetting contact and complete non-wetting contact, respectively. If the model which considers the pore size distribution (PSD) is used, AAD% decreases from 9.98% to 5.79%. The results of this study show that at temperatures below the temperature of quadruple point, assumption of a cylindrical contact leads to much more accurate predictions in the I–H–V region even when the pore size distribution is not considered.

1. Introduction

Gas hydrates or clathrate hydrates are crystalline ice-like compounds in which gas molecules of appropriate size and shape occupy the cavities formed by water molecules connected by hydrogen bonds. Hydrates usually form at high pressures and moderate temperatures (or low temperatures and moderate pressures). The size ratio of the gas guest component to the cavity determines the stabilized cage type, and therefore, the type of hydrate structure (Sloan and Koh, 2008). A concise review on gas hydrates can be found in the book by Sloan and Koh (2008). Hydrate formation in the oil and gas industry, such as pipelines and valves, has been shown to cause serious difficulties. Natural hydrates that form in permafrost regions or in deep ocean sediments are of great interest. Natural hydrates can play important roles in energy and environmental fields. Huge amounts of natural gases exist as hydrates in permafrost regions (Cherskii and Makogon, 1970; Davidson et al., 1978) or in subsea floor sediments in outer continental edges (Kvenvolden and McMenamin, 1980). Because each unit volume of hydrate contains approximately 170 unit volumes of gas at standard temperature and pressure, natural hydrates are classified as unconventional energy resources that may be useful in future (Kvenvolden, 1999; Sloan and Koh, 2008). Fears regarding global warming suggest that natural gas hydrates can dissociate and release their trapped gases as the temperature of oceans and atmosphere increase. The released gases may, in turn, escalate the abundance of greenhouse gases in the atmosphere and thus creates the potential for more gas hydrates to dissociate. This cycle is known as the "clathrate gun hypothesis" (Kennett et al., 2003; Maslin et al., 2004). Conversely, CO_2 hydrate formation/sequestration within deep ocean waters and sediments is also a significant aspect of how gas hydrates may play a role in global climate changes (Nakano et al., 1998; Ohgaki et al., 1996; Teng et al., 1997). It is essential to understand the effect of porous media on hydrate

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http://dx.doi.org/10.1016/j.jngse.2013.06.003

phase behavior in order to exploit trapped gas found in natural hydrate fields as well as potentially sequester carbon dioxide gas in sediments of oceans as natural hydrates.

Clarke et al. (1999) and Henry et al. (1999) were the first to model hydrate formation in porous media. They included a capillary term within the equation for hydrate equilibria within the bulk phase to account for the effect of pores on the activity of water. Many authors have modeled (Klauda and Sandler, 2001; Wilder and Smith, 2002; Wilder et al., 2001a, 2001b) and experimentally measured (Handa and Stupin, 1992; Smith et al., 2002; Seshadri et al., 2001; Uchida et al., 2002, 1999) gas hydrate equilibria in porous media. Based on the solid-solution model, the stability of gas hydrates depends directly on the activity of water (van der Waals and Platteeuw, 1959). Clarke et al. (1999) showed that capillary forces within the pores decrease the activity of water. As a result, hydrates will form at higher pressures in constant temperature conditions or at lower temperatures in constant pressure conditions in comparison with the bulk phase. This shift of equilibrium line, is also observed in systems containing inhibitors due to the fact that the geometrical constraints and inhibitors decrease the activity of water (Sloan and Koh, 2008).

The solubility of methane in the water phase is negligible and the models used to calculate the phase behavior of methane gas hydrates in porous media are based on the equality of the chemical potential of water in the water phase and hydrate phase. Consequently, it is reasonable to assume that the only difference between modeling the bulk and the porous media originates from the calculation of the activity of water. Results for bulk predictions are quite accurate. However, a thorough understanding of the different parameters affecting the capillary term including (1) surface tension, (2) shape factor and (3) wetting angle, is necessary for accurate modeling in porous media. Within this study, two different types of thermodynamic modeling are applied to predict the phase behavior of methane gas hydrates in porous media. The first model, developed by Clarke et al. (1999) is based on the equality of chemical potential of water in the hydrate phase and the liquid phase. This model assumes a single-size porous media and neglects the pore size distribution. The second type of thermodynamic model, developed by Klauda and Sandler (2001), is based on the equality of water fugacity in the hydrate phase and water phase. Unlike the first model, the second model considers the pore size distribution in the porous media. Once thermodynamic models are established, they are used to investigate the way, different parameters affect the capillary term. Different values of surface tension reported in literature are used along with the first thermodynamic model to understand which reported surface tension leads to the most accurate predictions. To further understand the parameters of the capillary term including shape factor and wetting angle, thermodynamic models are coupled with an optimization program (Genetic Algorithm) to obtain the optimized parameters that lead to the most accurate predictions. In order to assess the accuracy of the obtained optimized shape factors, these factors are correlating to the hydrate formation temperature and implemented for phase behavior predictions of an additional set of temperature–pressure experimental data. The results of thermodynamic modeling using the correlated shape factors are compared to the original model which assumes an ideal contact surface.

2. Thermodynamic model

2.1. Single-size modeling

For the single-size model, a uniform porous media containing pores of identical size and shape is assumed, thus, the pore size distribution can be neglected. The equality of chemical potentials of different species, μ_i, in all the phases (Liquid, Hydrate and Vapor) is the criterion for equilibrium and is identified in Equations (1) and (2).

$$\mu_i^L = \mu_i^V \quad (i = 1 \ldots N) \tag{1}$$

$$\mu_i^H = \mu_i^V \quad (i = 1 \ldots NF) \tag{2}$$

where N is the number of all components which exist in both vapor and liquid phases at equilibrium and NF is the number of components which form the hydrate phase. Since the water concentration in the vapor phase at the hydrate formation conditions is negligible, the criterion of equilibrium for water becomes:

$$\mu_W^H = \mu_W^L \tag{3}$$

The van der Waals–Platteeuw model (1959), which is a modification of classical adsorption statistical mechanics, is used to calculate the chemical potential of water in the hydrate phase. Van der Waals–Platteeuw model assumes that the hydrate lattice size is constant and independent of the gas molecule that occupies the cavities in a specific hydrate structure. As a result of this assumption, the chemical potential of water in a hypothetical empty cavity is equal for all gas species that occupy a specific hydrate structure. Assumptions included within the van der Waals–Platteeuw model, indicate that large molecules (which may distort the hydrate lattice) and asymmetric molecules (which might have restricted rotations inside the cavities) are not good applicants for the van der Waals–Platteeuw model. Another limitation of this model is that it considers only the first shell of water molecules in calculations of guest–host interactions and neglects the interaction energies associated with the second and third shells. According to the van der Waals–Platteeuw approach (1959), chemical potential of water in the hydrate phase is given as:

$$\mu_W^H = \mu_W^{MT} - RT_f \sum_{m=1}^{2} \upsilon_m \ln\left(1 + \sum_{J=1}^{NH} C_{mj} f_j\right) \tag{4}$$

where μ_W^{MT} is the chemical potential of water in a hypothetical empty cavity, R is the universal gas constant, T_f is the hydrate formation temperature, υ_m is number of type i cavities per water molecule, and f_j is the fugacity of any species in the vapor phase. f_j is calculated using the Soave–Redlich–Kwong (SRK) equation of state and is equal to the fugacity of that species in the hydrate phase due to the isofugacity criteria required by equilibrium conditions (Clarke et al., 1999). SRK is a modification of Redlich–Kwong equation of state that can accurately and easily represent the relationship between pressure, temperature, and phase composition. SRK relies on the critical properties and acentric factor to obtain its parameters in the equation.

Next parameter in Equation (4), C_{mj} is the Langmuir constant. According to Sloan and Koh (2008), the two major assumption used in calculating the Langmuir constant include, firstly, that the internal motion partition function of the guest molecule is the same of that of an ideal gas, and, secondly, that the potential energy of a guest molecule at a distant r from the cavity center can be represented by the spherically symmetrical potential $\omega(r)$ proposed by Lennard-Jones and Devonshire. The value of the Langmuir constant for any gas in any cavity depends upon the potential interaction between the lattice molecules and the trapped gas inside the cavity. In this work, Lennard-Jones 6–12 pair potential is used to calculate the potential interaction (Sloan and Koh, 2008) by: