Prediction of phase stability conditions of gas hydrates of methane and carbon dioxide in porous media

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A B S T R A C T

With the growing need to explore non-conventional energy sources, the hydrates of natural gases offer a realistic solution in the need for alternative energy sources. Gas hydrates are typically entrapped in the porous media showing sensitive phase stability conditions. Models for phase stability for gas hydrate have not yet been extensively investigated for porous media and thus need attention. In this paper, the phase stability model is developed from the basic Chen and Guo model (*Chem Eng J*, 1998, 71:145) to accurately predict the phase behavior of the clathrate hydrates of CH_4 and CO_2 in porous media of varying pore sizes from 6 nm to 100 nm which mimics the naturally occurring porous environment. We also propose a new equation for calculating the activity of water in porous media as a function of the pore size, the wetting angle, the surface tension, and the shape factor of the pores for varied temperature conditions. The model results are validated against experimental data available in open literature and found satisfactory. The proposed model uses very *few* input parameters (data intrinsic) and thereby is very beneficial in predicting the stability of the hydrates in virgin gas reservoirs wherein the characteristics of the gas reservoir are largely unknown. The developed model may further be applied to the hydrate systems of other natural gases in porous medium with suitable modifications.

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1. Introduction

Clathrate compounds or gas hydrates are non-stoichiometric crystalline compounds with snowy-ice like structures consisting of mainly hydrogen bonded network of host water molecules and entrapped guest molecules of gases such as methane (CH_4), ethane (C_2H_6), carbon-dioxide (CO_2), hydrogen sulphide (H_2S), etc. These hydrates have been found to provide a potential solution for gas storage and transportation, separation of flue gases and CO_2 sequestration and hence are of great importance. Massive reserves of natural gas hydrates already exist in the subsurface and seafloor sediments containing methane and thus shows potential source of energy for the future (Makogon, 2010). The gas hydrates are typically entrapped in the porous media and shows sensitive phase stability conditions with respect to surrounding characteristics of porous media such as temperature, pressure, salinity, etc. This calls for a robust reservoir model incorporating an efficient phase behavior model to predict the phase stability conditions of clathrate

to understand the formation and dissociation conditions of the gas hydrates in a better way.

Most of the existing thermodynamic models for predicting the phase behavior of gas hydrates are based on the three phase equilibrium in the bulk systems such as that of Parrish and Prausnitz (1972), Ng and Robinson (1976), Tohidi et al. (1995), Chen and Guo (1998), Ballard and Sloan (2002), Lee and Holder (2002) which are based on or are modifications of the vdW-P model. Till date, only few phase stability models have been developed which consider hydrate-gas two-phase equilibrium in porous media. Clennell et al. (1999) and Henry et al. (1999) developed a thermodynamic model predicting the three phase stability of CH_4 in marine sediments using the Gibbs−Thompson equation accounting for the increase in the incipient hydrate formation pressure by studying the effect of capillaries in the porous media. Klauda and Sandler (2001, 2003) proposed a model which predicted the distribution of methane hydrate in ocean sediments. In recent years, studies have shown contradicting results in the effect of surface textures and mineral components on the phase equilibrium of gas hydrates. For example, the experiments performed by Ruppel (1997) and Clennell et al. (1999) indicated that the pore size affects the equilibrium conditions of hydrates. The experiments of Handa and Stupin (1992),

Table 1
Details on the experimental data taken for model validation.

Gas hydrate system	Porous media	Pore sizes, nm	No. of data points	Temperature range, K	Pressure range, MPa	Reference
CH$_4$–H$_2$O	Silica gel	6–100	27	260–285	0–10	Handa and Stupin, 1992; Uchida et al., 2002; Kang et al., 2008
CO$_2$–H$_2$O	Silica gel	6–100	13	265–285	0–5	Kang et al., 2008

Table 2
Antoine constants for calculating Langmuir constants in Eq. (4).

Gas	$X \times 10^6$	Y	Z
CO$_2$	1.6464	2799.66	15.90
CH$_4$	2.3048	2752.29	23.01

Uchida et al. (1999, 2002), Zhang et al. (2002), etc., concluded that capillary force inhibits the formation of gas hydrates in narrow pores. Although, we agree that the surface texture does affect the nucleation and rate for hydrate formation *kinetically*, but the more recent experiments performed by Riestenberg et al. (2003) and Uchida et al. (2004) show that the surface textures and mineral components have only marginal effect on the phase stability of gas hydrates in porous media. The effect of solid surface on the hydrate phase equilibrium is still a matter of detailed investigations.

Although there are existing models predicting the phase behavior of gas hydrates in porous media, these need improvements. The aim of the present work is to, (1) present a more simplistic and accurate model which can be used extensively for gas hydrate reservoirs that are in the exploratory stages, (2) extend the existing work of Chen and Guo (1998) applicable to bulk hydrates and propose a model that accurately predicts phase equilibria of gas hydrates in porous media, (3) demonstrate the effect of porous medium over the phase equilibria for the gas hydrates of methane and carbon dioxide. In our previous work (Joshi et al., 2012) the Chen and Guo (1998) model was extended for the prediction of the phase stability of semiclathrate hydrates of gases. In this work, we have accounted for the effects of increase in the incipient hydrate formation pressure by incorporating the works of Yousif and Sloan (1991) and variations in pore sizes on the stability of gas hydrates in porous media. We have also incorporated the work of Klauda and Sandler (2001) by taking into account the shape factor of the pores and used in the model improving accuracy and the applications in the more realistic environment such as marine sediments.

2. Phase stability model

The Chen and Guo (1998) model used in this study proposes a two-step mechanism for the hydrate formation:

1. The quasi-chemical equilibrium for the reaction occurring in the process; $H_2O + \lambda_2 G \rightarrow G_{\lambda_2} \cdot H_2O$
2. The physical adsorption equilibrium for the filling of gas molecules in the linked cavities during the second step.

In this work, for the prediction of hydrate phase stability, the main components considered are, water phase, gas phase, hydrate phase. The Chen and Guo model is primarily a fugacity based approach for hydrate phase stability prediction and hence, our major focus has been on the two phase stability of gas and hydrate phase, by means of equating the fugacity of hydrate phase and the fugacity of the gas phase (Eq. (1)).

$$f = f^o(1 - \theta)^\alpha \tag{1}$$

where

$$\alpha = \frac{\lambda_1}{\lambda_2} \tag{2}$$

f^o is the fugacity of unfilled hydrate phase. The values of λ_1 and λ_2 are taken from open literature (Joshi et al., 2012) and are found to be 1.75 and 3, respectively. Based on the Langmuir adsorption theory 'θ' — the fraction of linked cavities occupied by gas molecules is calculated as shown in Eq. (3),

$$\theta = \frac{Cf}{1 + Cf} \tag{3}$$

The Langmuir constant 'C' is obtained as shown in Eq. (4).

$$C = X\exp\left(\frac{Y}{T - Z}\right) \tag{4}$$

The Langmuir constants are evaluated by integration of the two-parameter Lennard-Jones potential function are referred to the literature Sloan and Koh (2008). The fugacity of gas species 'f' is obtained using the Equation of State (EoS). Chen and Guo model uses the Patel–Teja (P–T) EoS to calculate the gas fugacity. In our previous work (Joshi et al., 2012) we have established that the SRK EoS is more useful in predicting the phase stability of gas hydrates at high pressure condition of above 5 MPa. Hence, in this study we incorporate the SRK EoS along with the hydrate model as shown in Eq. (5);

$$Z^3 - Z^2 + \left(A - B - B^2\right) - AB = 0 \tag{5}$$

Chen and Guo (1998) proposed that the fugacity of hydrates is obtained as a function of temperature, pressure and the activity of water as shown in Eq. (6).

$$f^o = f^o(T)f^o(P)f^o(a_w) \tag{6}$$

However, the above form of equation was applicable for bulk phase. It is observed that, in case of porous media, small pores, roughly less than 4 nm in average diameter and may be even larger create strain in the hydrate lattice which reduces the phase stability

Table 3
Antoine constants for calculating Langmuir constants in Eq. (8) for methane hydrates (this work).

Pore diameter, nm	A'	B'	C'
6	5.2602×10^{23}	−13,110	4.08
7	1584.40×10^{10}	−6241.43	27.04
10	5.2602×10^{23}	−13,315	4.08
30	5.2602×10^{23}	−13,510	4.08
50	5.2602×10^{23}	−13,555	4.08
100	5.2602×10^{23}	−13,600	4.08

Table 4
Antoine constants for calculating Langmuir constants in Eq. (8) for carbon dioxide hydrates (this work).

Pore diameter, nm	A'	B'	C'
6	3.4474×10^{23}	−14,080	6.79
30	3.4474×10^{23}	−14,255	6.79
100	3.4474×10^{23}	−14,295	6.79