



Modeling gas hydrate-containing phase equilibria for carbon dioxide-rich mixtures using an equation of state



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ABSTRACT

Thermodynamic modeling of phase behaviors for CO₂-rich mixtures in gas hydrate forming conditions are required for the process design in the field of carbon dioxide sequestration and enhanced oil recovery. With recent experimental data published for solubility of water in CO₂-rich mixtures that are significantly different from those previously published, improved modeling studies become necessary for phase equilibria containing gas hydrates. In the present study, an equation of state based on hydrogen-bonding nonrandom lattice fluid theory was applied for both vapor and liquid phases. The model for hydrogen-bonding contribution is simplified and a weak hydrogen bonding between water and carbon dioxide was included for improved calculation of mutual solubility. Hydrate phase was modeled by van der Waals and Platteeuw method but without guest specific parameters other than Kihara potential parameters. The method was applied to single and binary CO₂-rich guest mixtures containing methane, ethane, propane, isobutene, nitrogen, hydrogen sulfide and methanol for temperatures above 180 K and pressures below 100 MPa. Results of two- and three-phase equilibrium calculations containing gas hydrates were found to be comparable with those of CSMGem (Sloan and Koh, *Clathrate and Hydrates of Natural Gases*, 3rd ed., CRC Press, Boca Raton, FL, 2008) in general and better for water contents in liquid carbon dioxide in equilibrium with gas hydrates.

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1. Introduction

Thermodynamic phase behaviors of CO₂-rich mixtures in gas hydrate forming conditions are essential information for flow assurance in the field of carbon dioxide sequestration and enhanced oil recovery. Gas hydrates are formed in water-containing mixtures and may result in line plugging depending on process conditions such as temperature, pressure and water contents when guest species are present. For a given temperature incipient hydrate forming pressure is determined, below which no gas hydrates are formed. A mixture at hydrate forming temperature and pressure conditions may form gas hydrates depending on its water content. Water-containing mixtures in pipelines are often in hydrate forming temperature and pressure conditions. Thus the practical problem of flow assurance is to determine the limit of water contents below which no gas hydrates are formed. The limit turns out to be

the water contents of vapor or guest-rich liquid mixtures in equilibrium with gas hydrates. Thermodynamic data and models provide such information. Comprehensive equilibrium conditions including compositions may be conveniently calculated using CSMGem [1] in which a cubic-type EOS is used for guest-rich phase, a separate equation of state with excess Gibbs function model is used for aqueous phase and van der Waals-Platteeuw contribution is included with Kihara potential parameters and temperature and pressure dependent molar volume of empty hydrate for hydrate phase, both of which are specific to guest species.

Gas hydrate containing phase equilibria involve hydrate (*H*), vapor (*V*), water-rich liquid (*L_w*), guest-rich liquid (*L_g*) and/or Ice (*I*). Equations of state have been used for both vapor and liquid phases in recent modeling studies of hydrate containing phase equilibria such as a lattice EOS in Yang et al. [2,3] with association contribution, SAFT in Li et al. [4], cubic EOSs in Yoon et al. [5] and Bandyopadhyay and Klaua [6] with GE-EOS mixing rules but without association term and CPA EOSs in Folas et al. [7], Youssef et al. [8], Haghghi et al. [9], Chapoy et al. [10,11], and Karakatsani and Kontogeorgis [12]. Yang et al. [2,3] included self-association

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contribution of water molecules and applied their method to single guests of CO₂ [2] and methane [3] in calculating of two- and three-phase equilibria. Li et al. [4] included self and cross association contribution of water and alcohol inhibitors and applied their model to incipient hydrate forming conditions of single guest inhibitor systems and mixed guests. Chapoy et al. [10] introduced hydrogen-bonding of CO₂ between themselves and with water to obtain good agreements with solubility data in guest-rich liquid in equilibrium with gas hydrates and incipient hydrate forming conditions over a wide range of temperature from below freezing temperature of water. Chapoy et al. [11] later applied similar method for CO₂-rich mixtures containing impurities and compared with their data. Karakatsani and Kontogeorgis [12] found that their calculation significantly underestimated water contents in CO₂-rich liquid in equilibrium with gas hydrates assuming no hydrogen-bonding of CO₂.

In modeling gas hydrate phase van der Waals and Platteeuw model [13] is used for guest inclusion contribution and properties of empty gas hydrates. Langmuir constants for van der Waals-Platteeuw contribution were calculated using spherical core Kihara potential as done in Yoon et al. [5] and Chapoy et al. [10] and correlated as done in most other studies. Separately correlated Langmuir constants tend to increase the fitting degree of freedom. Incipient hydrate forming conditions were modeled in all these studies but limited to single guest systems in some studies [2,8]. Water contents were calculated in Yang et al. [2], Folas et al. [7], Chapoy et al. [11] and Karakatsni and Kontogeorgis [12].

Modeling studies rely on consistency of data as well as soundness of model. Large uncertainties are suspected in some data sets for hydrate containing H–L_g and L_w–H–L_g phase equilibrium and became major difficulties in developing a reliable method of calculation. Water contents in guest-rich phase provide key information for flow assurance together with incipient hydrate formation condition. For example strong pressure dependence of water contents in H–L_g equilibria for CO₂-water mixtures [14] was suspected to have large uncertainties [15]. Recent literature data show much weaker pressure dependence [11,15,16]. Data sets on L_w–H–L_g equilibria tend to show deviations between themselves including the quadruple point data.

Considering that recent modeling studies are less comprehensive and that recent water contents data in CO₂-water mixtures are significantly different from existing data, a new comprehensive modeling study for incipient hydrate forming conditions and water contents in guest mixtures is warranted for CO₂-rich mixtures. An equation of state approach with association contribution is expected to be applicable to both vapor and liquid phases. Guest independent molar volume of empty hydrates as opposed to those used in CSMGem [1] and Langmuir constants calculated from Kihara potential would simplify the nature of model. The present study is intended to develop a model and parameter sets for comprehensive and improved phase equilibria of CO₂-rich mixtures.

2. Thermodynamic relations

2.1. Van der Waals-Platteeuw model for gas hydrate phase

Phase equilibrium calculation requires equality conditions of chemical potential or fugacity for each component in all stable phases. When Helmholtz free energy is represented by its canonical variables, chemical potential representation is readily obtained. Chemical potential and fugacity may be used interchangeably using relation for a component in fluid phase;

$$f_i = \exp \left[\frac{\mu_i - \mu_i^{ig,0}}{RT} \right] \quad (1)$$

where the second quantity in the numerator denotes chemical potential of pure ideal gas at 1 bar. Eq. (1) can be applied to fugacity of water in hydrate phase to give,

$$f_W^H = \exp \left[\frac{\mu_W^{EH} - \mu_W^{ig,0}}{RT} + \frac{\mu_W^H - \mu_W^{EH}}{RT} \right] = \exp \left[\frac{\Delta\mu_W^{EH}}{RT} \right] \exp \left[\frac{\Delta\mu_W^H}{RT} \right] \quad (2)$$

The difference of chemical potential in the first exponential term is pressure corrected Gibbs free energy change of forming empty hydrates from pure water at ideal gas state. The exponential term represents the fugacity of empty hydrates that is written in terms of saturated vapor pressure and molar volume of empty hydrates.

$$f_W^{EH} = P_W^{EH} \phi_W^{EH} \exp \left[\frac{1}{RT} \int_{P_W^{EH}}^P V_W^{EH} dP \right] \quad (3)$$

The change of chemical potential in the second exponential term on the right hand side of Eq. (2) denotes the effect of guest inclusion into hydrate lattices that is represented by van der Waals and Platteeuw model [13];

$$\Delta\mu_W^H = RT \sum_i v_i \ln \left[1 + \sum_j C_{j,i} f_j^H \right] \quad (4)$$

where, v_i is the number of i -type cavity per water molecule, f_j^H is the fugacity of guest component j in equilibrium with fluid phase Π . $C_{j,i}$ is the Langmuir constant of guest component j in i -type cavity. v_i and $C_{j,i}$ depend on hydrate structure types; sI, sII and sH. The Langmuir constant is obtained using the spherical core Kihara potential between water and guest molecules.

$$U(r) = \begin{cases} \infty & \text{for } r \leq 2a_j \\ 4\epsilon_j \left[\left(\frac{\sigma_j - 2a_j}{r - 2a_j} \right)^{12} - \left(\frac{\sigma_j - 2a_j}{r - 2a_j} \right)^6 \right] & \text{for } r \geq 2a_j \end{cases} \quad (5)$$

where, σ_j is the core distance at zero potential, a_j is the radius of the spherical core, r is the distance of the guest molecule from the cavity center and ϵ_j represents the maximum attractive potential. For Kihara potential, McKoy and Sinanoglou [17] obtained the cavity potential for the interaction between water and the guest molecule in gas hydrate.

$$C_{j,i} = \frac{4\pi}{kT} \int_0^{R_i - a_j} \exp \left[-\frac{W(r)}{kT} \right] r^2 dr \quad (6)$$

$$W(r) = 2z_i \epsilon_j \frac{R_i}{r} \left[\left(\frac{\sigma_j}{R_i} \right)^{12} \left(\delta_j^{10} + \frac{a_j}{R_i} \delta_j^{11} \right) - \left(\frac{\sigma_j}{R_i} \right)^6 \left(\delta_j^4 + \frac{a_j}{R_i} \delta_j^5 \right) \right] \quad (7)$$

$$\delta_j^N = \frac{1}{N} \left[\left(1 - \frac{r}{R_i} - \frac{a_j}{R_i} \right)^{-N} - \left(1 + \frac{r}{R_i} - \frac{a_j}{R_i} \right)^{-N} \right] \quad (8)$$

where, R_i is the radius and z_i is the coordination number of i -type

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