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The importance of liquid phase compositions in gas hydrate modeling: Carbon dioxide–methane–water case study

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ABSTRACT

Liquid compositions obtained through vapor + liquid + hydrate equilibrium modeling are often neglected and not reported in literature. This work demonstrates the sensitivity and importance of the liquid phase compositions on selected models and parameters. The equations of state used to model two-phase systems are the Soave–Redlich–Kwong, the Valderrama–Patel–Teja and the Trebble–Bishnoi equations of state. The modeling analysis for three-phase systems is based on the Trebble–Bishnoi equation of state along with the model by van der Waals and Platteeuw. The vapor + liquid equilibrium model predictions at gas hydrate formation conditions were found to be greatly dependant on the liquid phase compositions. At the three-phase equilibrium, small modifications in the equation of state's interaction parameters significantly affected the liquid composition predictions while leaving the vapor compositions mostly unchanged. Lastly, the interaction parameters were optimized for the two phases separately using vapor + liquid equilibrium data. When optimized only for liquid, vapor and liquid compositions were predicted correctly. However, when optimized only for vapor, liquid compositions failed to fit experimental data.

1. Introduction

Gas hydrates, or clathrate hydrates, are non-stoichiometric crystalline compounds that arise from a gas or volatile liquid being encapsulated by water molecules. The guest molecules must be of correct size to fit inside and stabilize the crystal lattice via weak van der Waals forces with the host water molecules [1]. Gas hydrates usually form at moderate temperatures (0–25 °C) and high pressures (above 1 MPa). There are over 180 different molecules that form gas hydrates, the most notable being methane, ethane and carbon dioxide which are of particular interest for industrial applications [2]. Gas hydrates were first documented in 1810 by Sir Humphrey Davy and became relevant for the oil and gas industry in the 1930s because they were found to cause blockages in natural gas transmission lines [3]. Academic interest in the field then increased significantly and focused mainly on predicting hydrate formation conditions and inhibiting hydrate formation. The next turning point in hydrate research was the discovery during the 1960s of *in situ* natural gas hydrates in Siberian permafrost [4], which branched into research on gas hydrate exploitation as a potential energy resource. Current conservative estimates propose that the amount of energy stored in natural gas hydrate deposits, which predominantly consist of methane gas, is double the amount of all the other fossil fuel combined [5]. The enormous quantities of methane stored as metastable hydrates also pose an environmental issue as methane is a strong greenhouse gas [6]. Hydrates are also being investigated as an alternative to liquefied natural gas for transportation and storage purposes [7].

The accurate prediction of gas hydrate formation conditions is vital to industrial applications as hydrates can form inside pipelines thereby creating a hazard to flow assurance. Equilibrium data is available but it is experimentally time-intensive to acquire and limited to very specific conditions and components. Moreover, liquid compositions in hydrate systems are difficult measurements to obtain and are consequently scarce in literature. Due to these limitations, modeling from a thermodynamic perspective, is essential to rapid and accessible determination of equilibrium conditions [8]. Gas hydrate phase equilibria temperatures, pressures and compositions can be predicted using the model of van der Waals and Platteeuw to incorporate the hydrate phase and any typical thermodynamic method to model the vapor and liquid phases [9]. The vapor and liquid phases are most often represented by an equation of state (EoS) model, of which there are hundreds, each with its own advantages and disadvantages [10]. Classical cubic equations of state for gas hydrate modeling include the Soave–Redlich–Kwong [11] and Peng–Robinson EoS [12]. These models make use of pure components' parameters regressed from

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experimental values of vapor pressure and liquid density. As mixtures are always present at the three-phase equilibrium (water and a minimum of one gas hydrate former), binary interactions parameters (IPs) need to be included in the equation of state model to account for the interactions between different molecules. Using a two-phase flash algorithm, these parameters are regressed from vapor + liquid equilibrium (VLE) data for each specific mixture. This demonstrates the strength of this method as it utilizes binary vapor + liquid equilibrium data to predict multi-component vapor + liquid + hydrate equilibrium. The authors use the Trebble–Bishnoi EoS [13,14] as it contains four binary interaction parameters (k_a, k_b, k_c, k_d) which is more than classical EoSs and therefore is better suited to predict the non-ideal behavior when polar compounds such as water are present. The Soave–Redlich–Kwong [11] and the Valderrama–Patel–Teja EoS with NDD mixing rules [15–18] are used for one exercise in order to demonstrate that the choice of EoS had no consequence on the results obtained in this case study.

Gas hydrate systems always consist of water in combination with one or more gas molecules. Condensed phases, like liquid water, contain non-ideal effects as a result of the interaction between different molecules. Under vapor–liquid–hydrate forming conditions, the liquid phase is far less ideal than the vapor phase, which results in liquid compositions being more complex to model. The liquid phase is the reason why binary interaction parameters have a significant role in gas hydrate modeling. These parameters facilitate the fit of the liquid phase composition and ultimately dictate the equilibrium. Consequently, it is critical to show that liquid phase compositions fit experimental data to confirm a model's validity. The motivation behind this paper is that several gas hydrate modeling papers only report equilibrium conditions (temperature and pressure) and the vapor phase compositions but do not report the liquid phase compositions [19–26]. It is assumed that the lack of experimental solubility data is the main reason for this although other reasons are possible such as a poor fit of the liquid phase. The objective of this paper is to demonstrate the importance of considering the liquid phase composition when modeling gas hydrates equilibrium. The sensitivity of the different phases is analyzed with respect to different input parameters and it is shown that the predicted liquid phase composition can sometimes be erroneous while the predicted vapor phase composition and equilibrium temperature and pressure are correct. In gas hydrate applications, liquid compositions are more important than vapor compositions since they define the driving force for hydrate growth [27,28]. In general, crystallization processes use liquid compositions to define crystal growth [29]. The liquid compositions are also a very important parameter of gas hydrate formation in sediments [30,31]. When assessing the exact amount of gas stored in hydrate deposits, the gas solubility is a crucial factor in the calculations. Lundgaard and Mollerup [32] demonstrated that the solubility of the guest molecule significantly influenced the gas hydrate dissociation pressure. To show the significance of modeling using the liquid phase, the system selected in this study is the carbon dioxide + methane + water and vapor + liquid + hydrate system. Applications of this hydrate system include flue gas separation and carbon dioxide sequestration [33,34]. In this paper the technique of modeling three-phase gas hydrate equilibrium is first explained. Following this, the sensitivity and importance of the liquid phase compositions are evaluated for several cases studied.

2. Theory

For the three-phase, vapor + liquid + hydrate equilibria, the basic thermodynamic equations for the equilibrium condition are the equality of chemical potentials, μ_i^π, in all phases π:

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

where N is the total number of components in the system and μ is the chemical potential.

The fugacity and chemical potential of a component in the liquid and vapor phase can be calculated from a suitable equation of state. In this study the Trebble–Bishnoi equation of state is used [13,14]. For the chemical potential of water in the hydrate phase, van der Waals and Platteeuw [9] proposed a model that has been modified by Parrish and Prausnitz [35] to make it computationally efficient. The equation for the chemical potential of water in the hydrate phase is:

$$\mu_w^H = \mu_w^{MT} - RT\sum_{m=1} v_m \ln\left(1 + \sum_{j=1}^{NH} C_{mj}\hat{f}_j\right), \tag{2}$$

where $\hat{f}_j$ is the fugacity of hydrate former j, μ_w^{MT} is the chemical potential of water in the empty hydrate lattice, v_m is the number of cavities of type m per water molecule. C_{mj} is the Langmuir constant which is a function of temperature given by a correlation proposed by Parrish and Prausnitz [35] that is valid over the temperature in the range 260 K to 300 K.

The chemical potential difference of water in the empty hydrate lattice and the pure liquid state is:

$$\mu_w^{MT} - \mu_w^{L_o} = \Delta\mu_w^{MT-L_o}. \tag{3}$$

The right hand side of equation (3) is represented by the following equation from Holder *et al.* [36]:

$$\frac{\Delta\mu_w^{MT-L_o}}{RT} = \frac{\Delta\mu_w^0}{RT_0} + \int_{P_0}^{P} \frac{\Delta V_w^{MT-L_o}}{RT} \mathrm{d}P - \int_{T_0}^{T} \frac{\Delta h_w^{MT-L_o}}{RT^2} \mathrm{d}T. \tag{4}$$

The temperature dependent equation of the enthalpy is given below:

$$\Delta h_w^{MT-L_o} = \Delta h_w^0(T_0) + \int_{T_0}^{T} \Delta C_{Pw} \mathrm{d}T. \tag{5}$$

The last equation required is for the chemical potential of water in the liquid solution phase:

$$\mu_w^{sol} = \mu_w^{L_o} + RT\ln(a_w) \tag{6}$$

Combining equations (1) through (6) gives the following expression that is used to solve the hydrate chemical potential as shown by Bruusgaard *et al.* [37]:

$$\frac{\Delta\mu_w^{MT-L_o}}{RT_0} + \int_{P_0}^{P} \frac{\Delta V_w^{MT-L_o}}{RT} \mathrm{d}P - \int_{T_0}^{T} \frac{\Delta h_w^{MT-L_o}}{RT^2} \mathrm{d}T + \ln a_w = -RT\sum_{m=1} v_m \ln\left(1 + \sum_{j=1}^{NH} C_{mj}\hat{f}_j\right). \tag{7}$$

The parameters for the above equations are taken from the work of Holder *et al.* [36] except for a re-optimized value of $\Delta h_w^{MT-L_0}$ which was taken from Hashemi *et al.* [38].

For the equilibrium criteria to be respected, the component fugacities must be equal in all three phases. All components must be distributed in the system phases such that the total Gibbs energy is at a minimum. From thermodynamics, the total Gibbs energy is given by the following equation:

$$\underline{G} = \sum_{\pi}\sum_{i} n_i^\pi \mu_i^\pi, \tag{8}$$

where n_i^π is the molar amount of component i in phase π.

The system conditions are predicted by the minimization of energy using a flash technique. The temperature is initially fixed. Then, a pressure-search method is used to solve for the three-phase equilibrium condition. At each pressure, the two-phase flash is first solved (the requirement being equal component fugacities