



Application of equations of state to predict methane solubility under hydrate-liquid water two-phase equilibrium



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ABSTRACT

Gas solubility in water under hydrate-liquid water (H-L_w) two-phase equilibrium is the foundation of gas hydrate kinetic study. It is significant for the simulation of multiphase pipeline flow, the stability and amount evaluation of natural gas hydrate resources in deep water as well as gas storage and separation. In the current work, thermodynamic models were established by combining van der Waals-Platteeuw theory with PR, VPT and TB equations of state separately, named as Model VPR, VVPT and VTB, to predict methane solubility in water under H-L_w equilibrium. The Henry's law was also included for comparison. Available experimental data in literature were collected to test the applicability of these equations of state. In order to improve the predicting accuracy, binary interaction parameters in the asymmetric contribution term of non-density-dependent (NDD) mixing rules were modified. Good agreements between predicted and experimental data were obtained by Model VVPT with the modified NDD mixing rules.

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1. Introduction

Gas hydrates are non-stoichiometric crystalline compounds that consist of host water molecules forming hydrogen-bonded cages and guest gas molecules filling inside and stabilizing the crystal lattice by weak van der Waals forces [1]. Hydrate-forming gases can be methane, ethane, propane, carbon dioxide and so on. These gas molecules are suitable in size to be held in water cages. Low temperature and corresponding high pressure are basic conditions for gas hydrate formation.

When natural gases are exploited from oil or gas field in deep water, they are transported by multiphase pipelines under ambient temperature of about 4 °C and pretty high pressure. The high pressure from the inlet of transportation is essential to overcome the multiphase fluid flow resistance, as it is hard to set pressure-increasing equipment under deep water. Thus, gas hydrates are prone to form in subsea pipelines becoming big threat to safety flow assurance. Recent studies suggest that gas hydrates would block pipelines gradually after going through the stages of formation, migration and aggregation, leading to serious accidents [2–4].

Modelling gas hydrate phase equilibrium is necessary to prevent pipeline blockage.

Another significant aspect is that a large amount of natural gas hydrate resources exist in oceanic sediments, being regarded as possible energy source in the future [5]. One exploitation concept is to break hydrate solids into small pieces and pipe gas-water-hydrate three phases from seafloor to processing platform [6–10]. In this situation, the understanding of three-phase interaction regularities is crucial to evaluate development feasibility, which means to predict gas hydrate growth and dissociation rates accurately. Modelling gas hydrate-liquid water (H-L_w) two-phase equilibrium is the foundation of determining phase transition rate. Aspects such as utilizing gas hydrates to store and separate gas mixtures [11–14], analyzing hydrate stability in deep oceanic sediments and assessing exact amount of in situ gas hydrates are also occasions where gas hydrate kinetic study is truly required.

Many researchers have studied gas hydrate formation kinetics and established theoretical models to predict hydrate growth rate [15–21]. Among these models, the Skovborg & Rasmussen mass transfer model is widely used in multiphase flow conditions [3,4,22–25]. This model is a simplification of Englezos & Bishnoi intrinsic kinetic model [26,27]. The driving force of hydrate growth in this model is defined as the difference of gas concentrations in

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bulk liquid water and the H-L_w interface where two-phase equilibrium is reached. The gas dissolving ability in water under H-L_w equilibrium is also called gas solubility. However, according to Skovborg and Rasmussen [18] a 5%-error in the estimation of gas solubility can lead to the deviation of 14% in calculating hydrate formation driving force. Gas solubility in water under H-L_w equilibrium is such an important parameter that requests us to determine it accurately before predicting hydrate growth rate. More details about the importance of liquid phase compositions in gas hydrate modelling refer to the work of Servio et al. [28].

Both experiments and thermodynamic models have been used to determine gas solubility under H-L_w two-phase equilibrium. Yang et al. [29], Servio and Englezos [30] analyzed methane solubility in aqueous phase by sampling the fluid under H-L_w equilibrium state. The dissolved methane molecules in samples were expanded and collected in a high pressure chamber. The amount was determined by flash calculation or analytic flash technique. Seo and Lee [31] tested liquid phase compositions through gas chromatograph. Kim et al. [32,33] measured the solubilities of methane, ethane and carbon dioxide in hydrate-containing two-phase equilibrium system. Later, Lu et al. [34] measured methane solubility under H-L_w equilibrium by in situ Raman spectroscopy.

As for thermodynamic models, most workers [29,33,35–39] applied the van der Waals and Platteeuw theory (vdW-P) [40] to describe the H-L_w equilibrium. Fundamental assumptions behind this theory [40] include that (1) guest molecules would not change the shape of the crystal lattice, (2) one cage can hold no more than one guest molecule, (3) there is no interaction between guest molecules and (4) the classical statistical mechanics is applicable. In this theory, water chemical potentials in liquid water and hydrate phases are the same and vary with gas solubility. The original vdW-P model has been improved in different ways [1,41–44]. In our work, the combination of vdW-P theory, Holder model and Parrish-Prausnitz correlation [38,39] was selected. Difference lies in how to determine gas fugacity in liquid water. In general, approaches fall into three classes: (1) Henry's law [45] with the Poynting-type correction [37,46], (2) the equation of state (EoS) which can describe the strong polar aqueous with non-polar components, and (3) the activity coefficient model especially when hydrate inhibitions exit. However, few models can predict the gas solubility in water under H-L_w equilibrium accurately. The applicability of equations of state in this condition has not been evaluated.

When natural gas molecules dissolve in liquid water, it is a system with highly non-ideal aqueous and non-polar components. Ordinary classic cubic EoS with van der Waal's mixing rules usually cannot simulate this system well. So, other types of EoS, such as SAFT family (statistical association fluid theory), CPA (cubic plus association), CTS (cubic two-state) and their improved versions, were considered to calculate the thermodynamic properties of strong polar aqueous phases [47–49]. The problem is that even though these equations of state show excellent accuracy, they are not suitable for the numerical implementation in multiphase flow simulation, as they are usually computational time consuming [50].

Fortunately, several less common or modified cubic equations of state are reported to simulate liquid water phase effectively. For example, based on the modification of binary interaction parameters (BIPs), an improved Peng-Robinson equation of state (PR EoS) was developed to evaluate gas mixture solubility in water [50,51]. What's more, Valderrama modification of the Patel and Teja equation of state (VPT EoS) with non-density-dependent (NDD) mixing rules [52] and Trebble-Bishnoi equation of state (TB EoS) [53,54] are two typical models used in water and hydrate simulation. However, it is not clear which EoS has the better ability to predict gas solubility in water under H-L_w two-phase equilibrium.

The purpose of this study is to predict methane solubility in

water under H-L_w two-phase equilibrium, seeking an efficient calculation procedure to insert in the H-L_w multiphase flow simulation. In our work, the EoS is adopted to describe the liquid water phase because of its advantages in thermodynamic consistency and simplicity. The Henry's law is also included for comparison purpose. The main job is to investigate which EoS is better for simulating H-L_w system. Accordingly, the paper is organized as: (1) a brief description of the van der Waals-Platteeuw theory for hydrate equilibrium calculation, (2) a list of models to calculate gas fugacity in liquid phase, (3) simulation results comparison with all available experimental data in literature, (4) deviation analysis and BIPs modification in NDD mixing rules and finally (5) conclusions.

2. Theory

2.1. The van der Waals-Platteeuw theory

For water-hydrate two-phase equilibrium system, the water chemical potentials in liquid and hydrate phases should be equal:

$$\mu_w^L = \mu_w^H. \quad (1)$$

Taking the chemical potential of water in empty hydrate lattice μ_w^{MT} as a standard, Eq. (1) can be rewritten as:

$$\mu_w^{MT} - \mu_w^L = \mu_w^{MT} - \mu_w^H \quad (2)$$

$$\Delta\mu_w^{MT-L} = \Delta\mu_w^{MT-H}. \quad (3)$$

Based on the Langmuir adsorption theory, van der Waals and Platteeuw [40] proposed expressions to calculate the right hand side of Eq. (3):

$$\frac{\Delta\mu_w^{MT-H}}{RT} = - \sum_m v_m \ln \left(1 - \sum_j \theta_{mj} \right) \quad (4)$$

$$\theta_{mj} = \frac{C_{mj} f_j}{1 + \sum_k C_{mk} f_k} \quad (5)$$

where v_m is the number of type m cavities per water molecule in the lattice, θ_{mj} is the fraction of type m cavities occupied by gas component j , C_{mj} is the Langmuir constant which can be determined by Parrish-Prausnitz correlation [42]. The gas fugacity f_j in hydrate phase is a crucial parameter which equals to the value in hydrate-equilibrium phase. Here, the hydrate-equilibrium phase refers to the liquid water. Once the equilibrium is reached, fugacity of component j in all phases would be the same. Gas fugacity in liquid water is proportional to gas solubility, meanwhile affecting water-hydrate equilibrium state.

The left hand side of Eq. (3) is represented by Holder et al. [41] as:

$$\frac{\Delta\mu_w^{MT-L}(T, p)}{RT} = \frac{\Delta\mu_w^0(T_0, 0)}{RT_0} - \int_{T_0}^T \frac{\Delta h_w}{RT^2} dT + \int_0^p \frac{\Delta V_w}{RT} dp - \ln a_w \quad (6)$$

where $\Delta\mu_w^0(T_0, 0)$ is the chemical potential difference of water at standard state ($T = T_0, p = 0$), a_w is the activity of water given as $a_w = \gamma_w x_w$, γ_w is the activity coefficient of water which equals to 1.0 for pure water system, and x_w is the molar fraction of water in the aqueous phase. The molar fractions of water and dissolved gas added together are 1.0, that is $x_w + x_{CH_4} = 1$, when the dissolved gas

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