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Application of PRSV2 equation of state to predict hydrate formation temperature in the presence of inhibitors

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ABSTRACT

Three phases, hydrate–liquid water–vapor (H–L_w–V) equilibrium temperatures for the gas (single/mixture) hydrate in presence of inhibitors such as methanol (MeOH) and mono-ethylene glycol (MEG) have been predicted. The model is based on equality of water fugacity in the liquid water and hydrate phases. The van der Waals and Platteeuw model is applied for calculating the fugacity of water in the hydrate phase. The Stryjek and Vera modification of Peng–Robinson (PRSV2) equation of state is used to evaluate the fugacity of water in the vapor and liquid phases. To achieve more accurate results, binary interaction parameters are adjusted as a linear function of temperature. The Langmuir constants are demonstrated as a function of temperature by using genetic algorithm. Acceptable agreement between the model predictions and experimental data exhibits its reliability.

1. Introduction

Gas hydrates are crystalline solids which may be formed where small guest molecules and water are in contact at high pressure and low temperature condition. The water molecules comprise a lattice due to hydrogen bonding, and the lattice consists of many cages. Gas molecules occupy the cages, by means of that stabilizing the lattice which cannot exist without gas molecules [1]. Depending on the size and shape of the gas molecules, hydrates consist of three main structures named structure I (sI), structure II (sII) and structure H (sH), respectively [2]. In all three structures, typically there is only one gas molecule (guest) within each cage [2]. Hammerschmidt [3] determined that gas hydrates could block the gas transportation pipelines sometimes at temperature above the water freezing point. This discovery highlighted the significance of hydrates to the oil and gas industry and was an introduction to the modern research area. Gas hydrates are a very expensive problem in petroleum exploration and production operations. Gas hydrates can plug gas gathering systems and transmission pipelines subsea and on the surface. In offshore explorations, the main concern is the multiphase transfer lines from the wellhead to the production platform where low seabed temperatures and high operation pressures advance the formation of gas hydrates. The following are the thermodynamic methods to prevent the hydrate formation:

(1) Reducing the water concentration from the system.
(2) Operating at temperatures above the hydrate-formation temperature for a given pressure by insulating the pipelines or using heat.
(3) Operating at pressures below the hydrate-formation pressure for a fixed temperature.
(4) Adding inhibitors such as salts, methanol, and glycols to inhibit the hydrate formation conditions and move the equilibrium line to higher pressure and lower temperature.

Inhibitors are added into processing lines to inhibit the formation of hydrates. There are two kinds of inhibitors: thermodynamic inhibitors and low-dosage inhibitors [4]. The thermodynamic inhibitors have been applied for a long time in the industry and perform as antifreeze. Inhibitors such as ethylene glycol, methanol, and electrolytes inhibit hydrate formation. It is important to determine the inhibition effects of these additives to evade hydrate formation and select the best inhibitor for a given system and operating conditions. In order to determine the amount of inhibitor needed for inhibiting hydrate formation in natural gas pipelines and transportation equipment, it is important to predict reliably the hydrate formation conditions in the inhibitor containing systems. The knowledge of phase diagram and fluid properties is fundamental in petroleum and chemical engineering. It is necessary to have the more exact tool to calculate these properties. Different approaches and models can be taken into account, including activity models and equations of state. The latest have become needed in the modeling of Vapor–Liquid Equilibrium (VLE). Many developments have been presented to improve these models, and it is not easy to select the suitable model for a special case. In these mod-

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els, two general approach are common, the γ–φ and φ–φ. In these approaches, the solid solution theory of van der Waals and Platteeuw [5] is used for calculating the fugacity of water in the hydrate phase. The γ–φ approach is based on activity model for liquid water phase and an equation of state for the vapor phase. The φ–φ approach uses an equation of state for vapor and liquid water phase. Many thermodynamic models for phase equilibrium in the hydrate system containing inhibitors had been reviewed and discussed. These models are based on the theories of statistical thermodynamics and the equality of water chemical potential in all phases [1,2,5]. Anderson and Prausnitz [6], Munck et al. [7], and Du and Guo [8] applied γ–φ model for evaluating water fugacity in liquid Phase and used Redlich–Kwong (RK) EOS, Soave–Redlich–Kwong (SRK) EOS, and the modified Peng–Robinson (m-PR) EOS, respectively to calculate the fugacity of water in the vapor phase. On the other hand, the φ–φ model can be used in wide ranges of temperature and pressure. In order to enhance the ability of the φ–φ model in the prediction of hydrate formation conditions, some works have been published in recent years. Trebble–Bishnoi EOS was applied by Englezos et al. [9]. Extended Fürst–Renon electrolyte EOS was applied by Zuo et al. [10]. Ma et al. [11] used Patel–Teja EOS coupled with Kurihara mixing rules. Li et al. [12,13] used Statistical Associating Fluid Theory (SAFT) EOS in order to evaluate hydrate dissociation for single and mixtures gases.

The phase criteria in the van der Waals and Platteeuw model, is that the chemical potential of water in different phases must be equal. There are many reference energy parameters in the van der Waals and Platteeuw model that should be regressed to calculate the fugacity of water in the hydrate phase. Various authors have extended the van der Waals and Platteeuw model to improve the accuracy of the prediction. Instead of using the equality of the chemical potentials, they have chosen to solve the equality of the water fugacity in all phases. Sloan et al. [14] were the first to relate the fugacity of water in the hydrate phase to the chemical potential difference of water in the filled and empty hydrate. Klauda and Sandler [15] have also developed a modification of the van der Waals and Platteeuw model. Their approach is similar to the Sloan et al. approach. They proposed a new approach to calculate the cell potential and they have developed different correlations to estimate the values of the molar volume and the vapor pressure of the empty lattice. Chen and Guo [16,17], Zhang et al. [18], Martin [19] also proposed a fugacity-based model to describe fugacity of water in the hydrate phase.

To understand the inhibiting effect of alcohols or glycols on hydrate formation, it is important to predict the phase equilibrium condition in hydrate systems with inhibitors. It is reported that PRSV2 (Stryjek and Vera [20,21] Modification of Peng–Robinson) equation of state is superior in predicting Vapor–Liquid Equilibrium (VLE) for pure component. Many equations of state and different mixing rules has been used to predict gas hydrate formation condition while the ability of the PRSV2 equation of state with Margules-type two-binary-parameter mixing rule, in this field, is not studied yet. In this work, firstly the high pressure Vapor–Liquid Equilibrium (VLE) of natural gas components + water + polar inhibitor systems were modeled by the PRSV2 equation of state coupled with Margules-type two-binary-parameter mixing rule. Binary interaction parameters between typical natural gas components and hydrate inhibitors and water have been adjusted as a function of temperature. The based VLE model was then coupled with the hydrate model previously proposed by Klauda and Sandler and used to predict the hydrate formation temperature of various polar inhibitors containing systems. In Klauda and Sandler's work, different thermodynamic models are used for liquid and vapor phases, and three model parameters are needed in the calculation [15]. In this work PRSV2 equation of state coupled with Margules-type two-binary-parameter mixing rule has been used to model both liquid and vapor phase instead of using different model in these two phases. In this study, the Langmuir constants are exhibited as a function of temperature instead that evaluated by potential function. There are two to four parameters in evaluating the Langmuir constants, and the parameters are regressed by single and mixture guest's gas hydrate equilibrium data. Results of H–L_w–V phase equilibrium calculation show the present model improves other models in the literature in terms of average absolute percent deviation in temperature (AADT) and absolute average relative deviations in temperature (AARD-T) from experimental data.

2. Genetic algorithm

Many different optimization techniques have been proposed to estimate the adjustable parameters for the mixing rules [22–29] used behavior of VLE and LLE systems. But most of them to study the phase suffer from solution multiplicity and existence of multiple roots for binary interaction parameters when used to correlate the experimental data. The techniques that use the gradient-based methods, such as Gauss–Newton [22], Gauss–Marquardt [23], and sequential quadratic programming (SQP) methods [24], are conventional optimization techniques in the phase equilibrium calculations. Since the evaluation of gradients is one of the erroneous parts of these techniques, the simplex pattern search methods have been used to obtain the best values for the binary interaction parameter [25]. However, these methods cannot provide a theoretical guarantee of global optimality. In the recent years, new optimization techniques have been proposed based on the global optimization methods. Among them the interval [26,27], branch and bound methods [28] can be mentioned. Due to the rounding-errors produced in the computations using these methods, despite the strong theoretical basis, the results obtained are not definitely globally optimum results. Another shortcoming is that because of the need to the gradient evaluations, these methods have a higher error potential to produce. It should be noted that there are a few techniques that use the gradient less random search (RS) methods as the optimization engines [29]. These techniques are rarely used to study the phase behavior of VLE, VLLE and LLE systems. In this work a new technique that is based on the genetic algorithm, was used to study the phase behavior of hydrate forming system. More detail about Genetic Algorithm that used in this work can be founded in the literature [30].

3. Modeling

3.1. Phase equilibrium criteria

The fugacity-based approach is used in this paper to describe phase behavior of clathrate hydrates. At phase equilibrium, the fugacity of water is equal in all coexisting phases:

$$f_w^H(T,P) = f_w^\pi(T,P,\underset{\sim}{x}) = f_w^V(T,P,\underset{\sim}{x}) \tag{1}$$

where π is the liquid (L) phase, and $\underset{\sim}{x}$ is the molar composition and obtained from a flash calculation using the PRSV2 equation of sate. $f_w^H(T,P)$, $f_w^\pi(T,P,\underset{\sim}{x})$ and $f_w^V(T,P,\underset{\sim}{x})$ are the fugacity of water in hydrate phase, liquid water phase, and vapor phase, respectively at temperature T and pressure P. In this work, the fugacity of water in the vapor and liquid phase is calculated by the equation of state coupled with mixing rule, and the fugacity of water in the hydrate phase is calculated by the modified van der Waals and Platteeuw model.