Prediction of phase equilibrium conditions for gas hydrates formed in the presence of cyclopentane or cyclohexane

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ABSTRACT

In this work, we predicted the hydrate formation conditions for the pure and mixed gas systems of CH_4, N_2, O_2 and CO_2 in the presence of cyclopentane or cyclohexane. Chen-Guo model coupled with the predictive Soave-Redlich-Kwong (PSRK) group contribution method was used to calculate the three-phase equilibrium, and the UNIFAC model was employed to calculate the activity coefficient of the liquid phase. The pressure-corrected Henry's law was employed to calculate the mole fraction of gas components existing in the aqueous phase except water. The prediction results and the percent of Absolute Average Deviation for the calculated hydrate formation pressures and temperatures were presented. It was found that the results predicted in this work agree well with those reported in the literature. Cyclopentane and cyclohexane in aqueous phase was assumed to evaporate into the gas phase and may change the gas components and the corresponding mole fractions in the gas phase. However, the results showed that the concentration variation of cyclopentane or cyclohexane has slight impact on the hydrate formation thermodynamics.

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1. Introduction

Gas hydrates are non-stoichiometric crystalline compounds with clathrate structures formed by a lattice of hydrogen-bonded water molecules at high pressures and low temperatures. The hydrogen-bonded water cages are large enough to host small gas molecules, e.g. methane (CH_4), nitrogen (N_2), carbon dioxide (CO_2) and propane (C_3H_8). The ice-like structure enables and stabilizes the existence of gas hydrates at higher temperatures and elevated pressures. Gas hydrates are known to form in three common structures such as structure I (sI), structure II (sII) and structure H (sH), and they would form semiclathrate hydrate in the presence of quaternary ammonium salts. The difference among these structures is due to the cavity size and shape. The type of hydrate structures mainly depends on the molecular diameters of the guest molecules [1].

Gas hydrates are suggested to be utilized for various applications such as gas storage and transportation [2,3], gas separation [1,4], refrigeration [5], and so on. Also, vast quantities of gas hydrates existing in the permafrost and deep sea have been considered as a potential energy resource. However, gas hydrate has many disadvantages such as causing global-warming and blocking oil and gas pipelines [1]. In order to solve these problems, many researchers found that the addition of thermodynamic inhibitors is able to shift the hydrate formation conditions to higher pressures and lower temperatures. On the contrary, adding thermodynamic promoters could shift the hydrate formation conditions to lower pressures and higher temperatures, which are of great significance for the hydrate-based applications. It is known that the phase behavior of hydrates is complicated and difficult to analyze, which requires amounts of experiments and long time. Generally, the experimental measurements of hydrate phase equilibria are time-consuming and costly, so the prediction of hydrate phase equilibria using reliable and accurate predictive models are important.

Among the predictive models of three-phase equilibrium of gas hydrate, the van der Waals–Platteeuw (vdW-P) [6] and Chen–Guo [7,8] models are often used to calculate the hydrate formation conditions. These classic thermodynamic approaches are based on the fugacity equality among hydrate, liquid and gas phase. However, Chen-Guo model assumed the activity of water to be unity and

neglected the influence of gas solubility in aqueous phase. The solubility of acid gases (e.g. carbon dioxide and hydrogen sulfide), hydrocarbons and inhibitors/promoters in the aqueous phase may affect the water activity and change its value, and in this case the influence cannot be neglected [9–12]. Therefore, The G^e-EoS approach was proposed by Englezos and Bishnoi [13]. They pointed out that using suitable mixing rules could predict the complicated phase behavior of the hydrate systems effectively. In the hydrate systems containing inhibitors and sour gases, Ma et al. [14] used the Kuihara mixing rule coupled with the Wilson equation to calculate the water activity. Sun and Chen [9] combined the PT EoS with the Debye-Hückel electrostatic term to predict the nonideality of the aqueous phase. Herslund et al. [15] used a thermodynamic model and the cubic-plus-association equation of state to (EoS) model the systems containing THF (tetrahydrofuran), CP (cyclopentane) and their mixtures. The phase equilibrium data predicted by the model was in good agreement with the data measured in the experiments. As for the aqueous phase activity, the UNIQUAC model was constantly used by Anderson and Prausnitz [16], Munck et al. [17], Du and Guo [18] and Hajar Delavar and Ali Haghtalab [19]. For the calculation of the light gases and hydrocarbons in the aqueous phase, particularly for highly water-soluble components, i.e. CO_2, H_2S, Klauda and Sandler [11,12] employed the modified UNIFAC model and PSRV EoS coupled with the classical mixing rules. To the best of our knowledge, there is no literature focusing on the prediction of the hydrate systems containing cyclopentane or cyclohexane using the group contribution method.

The purpose of this work is to predict the hydrate formation conditions for the pure and mixed gas systems in the presence of cyclopentane (CP) or cyclohexane (CH), and the promoter volatility was considered to improve the prediction accuracy. In this work, Chen-Guo model coupled with the predictive Soave-Redlich-Kwong (PSRK) group contribution method [20–23] was adopted to predict the hydrate formation conditions. The UNIFAC model was applied to calculate the activity coefficient of the aqueous phase [24]. These models eliminated the need to empirically fit the intermolecular parameters that are required in the van der Waals and Platteeuw model. To increase the accuracy of the phase equilibrium calculations, the solubility of gases in aqueous phase was considered and calculated through the Henry's law. The PSRK approach was used to calculate the vapor phase fugacity. The Chen−Guo model was applied to model and calculate the fugacity of the hydrate phase. Also, the predicted results were compared with the experimental data reported in the literature.

2. Thermodynamic framework

In the prediction of gas hydrate formation conditions, water that exists in the three phases (vapor, water, and hydrate phase) is considered as the key component.

$$f_w^H(T, P) = f_w^L(x_w, T, P) = f_w^V(y_w, T, P) \tag{1}$$

where f_w^H, f_w^L and f_w^V are the fugacity of water in the hydrate, liquid and vapor phase, respectively; y_w and x_w represent the mole fraction of water in the gas and aqueous phase, respectively. The subscript w stands for water; f_w^V and f_w^L are calculated using the PSRK equation and the UNIFAC activity coefficient function, respectively. The fugacity of water in the hydrate phase, f_w^H, is expressed as

$$f_w^H(T, P) = f_w^{MT}(T) \times \exp\left(\frac{-\Delta\mu_w^{MT-L}}{RT}\right) \tag{2}$$

where f_w^{MT} represents the fugacity of water in the hypothetical

empty hydrate lattice and is assumed equal to the saturated vapor pressure of the empty hydrate lattice [25]; $\Delta\mu_w^{MT-L}$ is the chemical potential difference between the empty hydrate lattice and water in the aqueous phase, which is calculated through the method of Holder et al. [26]; and R is the universal gas constant.

2.1. Thermodynamic model of the gas phase

The PSRK group-contribution method is based on the SKR equation of state, the UNIFAC model is applied to calculate the activity coefficient, and the value of q_1 was modified for the purpose of obtaining more accurate results at high pressures [20]. In this study, the PSRK method is used to calculate the fugacity of components in the gas phase, as

$$P = \frac{RT}{v_m - b} - \frac{a}{v_m(v_m - b)} \tag{3}$$

where P, T and v_m are the system pressure, temperature and molar volume, respectively; a and b are parameters of PSRK EoS.

$$a_i = \frac{0.42748R^2T_{c,i}^2 f(T)}{P_{c,i}}, \quad b_i = \frac{0.08664RT_{c,i}}{P_{c,i}} \tag{4}$$

$$f(T) = 1 + c_1\left(1 - T_r^{0.5}\right)^2 \tag{5}$$

$$c_1 = 0.48 + 1.574\omega - 0.176\omega^2, T_r = \frac{T}{T_c} \tag{6}$$

where $P_{c,i}$ and $T_{c,i}$ stand for the critical pressure and critical temperature of pure component i, respectively; ω is the acentric factor. The PSRK mixing rule is written as

$$a = b\left[\frac{g_0^E}{A_1} + \sum y_i\frac{a_i}{b_i} + \frac{RT}{A_1}\sum y_i \ln\frac{b}{b_i}\right] \tag{7}$$

$$b = \sum y_i b_i \tag{8}$$

$$g_0^E = RT\sum y_i \ln\gamma_i \tag{9}$$

$$\frac{a}{bRT} = \frac{1}{A_1}\sum y_i \ln\gamma_i + \frac{1}{A_1}\sum y_i \ln\frac{b}{b_i} + \sum y_i\frac{a_i}{b_i RT} \tag{10}$$

where g_0^E is excess Gibbs energy; the recommended value of A_1 is −0.64663 in the PSRK model [20]; the activity coefficient of component i, γ_i is calculated using the UNIFAC model. Thus, the fugacity of coefficient is given by

$$\ln\varphi_i = \frac{b_i}{b}(z - 1) - \ln\left[z\left(1 - \frac{b}{v_m}\right)\right] - \sigma\ln\left(1 + \frac{b}{v_m}\right) \tag{11}$$

$$\sigma = \frac{1}{A_1}\left(\ln\gamma_i + \ln\frac{b}{b_i} + \frac{b}{b_i} - 1\right) + \frac{a_i}{b_i RT} \tag{12}$$

where φ_i is the fugacity coefficient of the pure component i; $z = PV/RT$.

This mixing rule can also be used to introduce other G^E models into the SRK equation of state. Fischer and Gmehling [21] pointed out that for any G^E model the parameters derived from vapor-liquid equilibria (VLE) can be used to enable reliable predictions of phase equilibria, whereby excellent results are usually obtained for a large temperature range.