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Explicit pressure dependence of the Langmuir adsorption constant in the van der Waals–Platteeuw model for the equilibrium conditions of clathrate hydrates

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ABSTRACT

In this work, we propose a new pressure- and temperature-dependent Langmuir adsorption constant for the modeling of the phase boundary of clathrate hydrates over a wide range of conditions. The proposed Langmuir adsorption constant is designed to produce a reduced free volume available to the encapsulated gas molecules as the pressure increases. We show that the combination of a cubic equation of state and the van der Waals–Platteeuw model with this new Langmuir model can be used to describe various types of three phase coexisting conditions of gas hydrates, from vapor–ice–hydrate equilibrium (VIHE) at low temperatures, to vapor–liquid–hydrate equilibrium (VLHE) at higher temperatures, and to liquid–liquid–hydrate equilibrium (LLHE) at high pressures, using a single set of parameters. The average relative deviations in the equilibrium pressure are found to be 4.57% for 12 pure gas hydrates over a large range of temperatures (148.8–323.9 K) and pressures (5.35×10^2 Pa to 8.27×10^8 Pa). Furthermore, the retrograde behavior observed in CH_4, CO_2, C_3H_8, and i-C_4H_{10} pure gas hydrate systems can all be successfully modeled by the change of free volume at high pressures. We believe that this method is useful for many gas hydrates related the multiple three-phase regions.

1. Introduction

Gas hydrates are a solid mixture of gas molecules and water, in which the water molecules are in specific arrangements that form cavities large enough to encapsulate small gas molecules. Depending on the size of the gas molecules, the gas hydrates may have three different types of crystallographic structures: structure I (e.g., methane, ethane, CO_2, etc.), structure II (propane), and structure H (mixture of methane and butane) [1]. Clathrate hydrates may be stable above the normal melting temperature of water by as much as 50 K at high pressures (at 531 MPa for methane hydrates). Recently, some experimental measurements indicated that some gas hydrates may be stable under extremely high pressures (e.g. several GPa [2–6]). Normally the melting temperature of gas hydrates increase with increasing pressure. However, at such high pressures, the melting temperature can decrease with increasing pressures, aka, the retrograde behavior [3,5]. The melting temperature, or the phase coexisting condition, represents the stability limit of the gas hydrates, and is critical for the exploration and exploitation of clathrate hydrate resources.

An accurate thermodynamic model could be very useful for understanding the stability and the phase transitions of gas hydrates under various conditions. A common approach for the modeling of phase equilibrium is the combined use of an equation of state (EoS) for the fluid phase and the van der Waals–Platteeuw (vdW–P) model for the solid phase [7]. Most of such models focuses on the modeling of one or two types of phase coexisting condition, e.g., the vapor–ice–hydrate (VIH), vapor–liquid–hydrate (VLH), or liquid–liquid–hydrate (LLH) equilibria [8–10]. Only few models can be used to describe the various type of phase behavior simultaneously. The challenge here is the need to properly describe molecular interactions and structures over a wide range of temperature and pressure conditions. Klauda and Sandler [11,12] developed a fugacity-based model that allows for modeling these three types of phase coexisting conditions simultaneously. In their approach, the change of the water cage structures with guest molecules, temperature, and pressure are taken into account by using a guest-dependent saturated vapor pressure of the empty hydrate lattice. Ballard and Sloan [13–16] proposed a chemical potential-based model with explicit considerations of the distortion of lattice according the absorbed gas molecules. Their model can be used to describe the retrograde behaviors observed in CH_4, CO_2, and C_3H_8 hydrates. The success of these models in the modeling of the retrograde behaviors is attributed to the inclusion of deformation of hydrate lattice with pressure. Klauda and Sandler

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adopted a guest-dependent empty hydrate lattice vapor pressure to account for the distortion of lattice [12]. Ballard and Sloan suggested the use of experimental density data for the solid hydrate phase for the correction of the lattice distortion [13].

In this work, we present a new approach for simultaneous modeling of the VIHE, VLHE, and/or LLHE of pure gas hydrates. In this method, the fugacity of a species in the fluid phase is determined by the Peng–Robinson–Stryjek–Vera (PRSV) EoS [17] combined with the predictive COSMO-SAC activity coefficient model [18] through the 1st order modified Huron-Vidal (MHV1) mixing rule [19]. This method, denoted as PRSV + MHV1 + COSMOSAC does not require input of any experimental data for the mixture fluids. In the solid hydrate phase, the fugacity is determined from the van der Waals and Platteeuw (vdW–P) model. In particular, the Langmuir adsorption constant is made pressure-dependent in order to recognize the deformation of the lattice at high pressures. We show that this approach is capable of modeling various types of gas hydrates (CH_4, C_2H_2, C_2H_6, C_3H_8, i-C_4H_{10}, CF_4, CH_3F, $CBrF_3$, $CBrClF_2$, CCl_2F_2, CCl_3F, and CO_2) from low temperature-low pressure VIHE, to VLHE, and to high temperature-high pressure LLHE. The retrograde behavior observed in 4 gas hydrates (CH_4, C_3H_8, i-C_4H_{10}, and CO_2) can also be modeled successfully. We believe that the new method is a simple yet powerful tool for modeling the phase behavior of gas hydrates over a wide range of conditions.

2. Theory

The three-phase coexisting condition of gas hydrate is determined based on the equality of fugacity of water in all three phases

$$\bar{f}_w^I(T,P,y_i) = \bar{f}_w^{II}(T,P,x_i) = \bar{f}_w^H(T,P,y_i) \tag{1}$$

where the superscripts I and II denote for the vapor, liquid, or ice phase; and superscript H denotes the solid hydrate phase. In the following we describe the determination of fugacity of water in various phases.

2.1. The fugacity in the fluid phase from the Peng–Robinson–Stryjek–Vera equation of state

The PRSV EoS describes the pressure–volume–temperature relation of a fluid as

$$P = \frac{RT}{\underline{V}-b} - \frac{a(T)}{\underline{V}(\underline{V}+b)+b(\underline{V}-b)} \tag{2}$$

where P is pressure, R is the gas constant, T is temperature, and $\underline{V}$ is molar volume. The variables a and b are species-dependent parameters and are determined from the critical properties of a pure fluid according to Stryjek and Vera's works [17,20]. For mixtures, the composition dependence of a and b values is determined by using the MHV1 mixing rule [19], that requires the liquid phase excess Gibbs energy from the EoS at zero pressure to be the same as that from a liquid model. In this work, the predictive liquid model without binary interaction parameters, the COSMO-SAC activity coefficient model [18], is used.

$$\ln\ \gamma_i = n_i \sum_{s}^{nhb,OH,OT} \sum_{\sigma_m} p_i^s(\sigma_m^s)[\ln\ \Gamma_S^s(\sigma_m^s) - \ln\ \Gamma_i^s(\sigma_m^s)] + \ln\frac{\Phi_i}{x_i} + \frac{z}{2}q_i\ \ln\frac{\theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i}\sum_j x_j l_j \tag{3}$$

where $\Phi_i = x_i r_i / \sum_j x_j r_j$, $\theta_i = x_i q_i / \sum_j x_j q_j$, and $l_i = (z/2)(r_i - q_i) - (r_i - 1)$. The r_i and q_i are the normalized volume and surface area parameters for species i, and z is the coordination number whose value is set to 10 in this work. $n_i = A_i/a_{eff}$ is the number of surface segments contained in species i, A_i is the surface area of species i, a_{eff} is the effective segment area, and $p_i(\sigma_m)$ is the σ-profile of a substance i. The σ-profile is the probability of finding a surface segment m with a screening charge density σ_m on the surface of species i. The σ-profile reflects the electronic nature of a chemical and is determined from first principle solvation calculation [21]. The $p_S(\sigma_m)$ is the σ-profile of the mixture calculated as

$$p_S^s(\sigma) = \frac{\sum_i x_i A_i p_i^s(\sigma)}{\sum_i A_i q_i} \tag{4}$$

The superscript s indicates surface from hydrogen bonding atoms, such as the hydroxyl group (OH) and any others (OT), or none hydrogen bonding (nhb) atoms. $\Gamma_j(\sigma_m)$ is the activity coefficient of segment with a charge density of σ_m in solution j (j is i for the pure liquid, or S for the mixture), and is determined from

$$\ln \Gamma_j^s(\sigma_m^s) = -\ln\left\{\sum_t^{nhb,OH,OT} \sum_{\sigma_n} p_j^t(\sigma_n^t)\Gamma_j^s(\sigma_n^t)\exp\left[\frac{-\Delta W(\sigma_m^s,\sigma_n^t)}{RT}\right]\right\} \tag{5}$$

where $\Delta W(\sigma_m, \sigma_n)$ is the electrostatic interaction between two segments of charge density σ_m and σ_n.

$$\Delta W(\sigma_m^t, \sigma_n^s) = c_{ES}(\sigma_m^t, \sigma_n^s)^2 - c_{hb}(\sigma_m^t, \sigma_n^s)(\sigma_m^t, \sigma_n^s)^2 \tag{6}$$

with interaction coefficients $c_{ES} = 6525.69 + 1.4859 \times 10^8\ \mathrm{T}^{-2}$, and

$$c_{hb}(\sigma_m^t, \sigma_n^s) = \begin{cases} 4013.78/(\mathrm{kcal\ \ mol^{-1}}\ \ \mathring{A}\ \ \mathrm{e^{-2}}) & \text{if } s=t=OH \text{ and } \sigma_m^t\cdot\sigma_n^s<0 \\ 932.31/(\mathrm{kcal\ \ mol^{-1}}\ \ \mathring{A}\ \ \mathrm{e^{-2}}) & \text{if } s=t=OT \text{ and } \sigma_m^t\cdot\sigma_n^s<0 \\ 3016.43/(\mathrm{kcal\ \ mol^{-1}}\ \ \mathring{A}\ \ \mathrm{e^{-2}}) & \text{if } s=OH,\ t=OT, \text{ and } \\ \sigma_m^t\cdot\sigma_n^s<0 & \\ 0 & \text{otherwise} \end{cases}$$

The details of the COSMO-SAC model, including the values of its parameters, can be found in Ref. [18].

2.2. The fugacity in clathrate hydrate from the van der Waals–Platteeuw model

The original van der Waals–Platteeuw model was developed to describe the chemical potential of water in the solid hydrate phase. Chen and Guo [8], and more recently, Klauda and Sandler [11] revised the original vdW–P equations to determine the fugacity of water in clathrate hydrates,

$$\bar{f}_w^H(T,P,y_l) = f_w^\beta(T,P)\exp\left(\sum_m \nu_m \ln\left(1-\sum_l \theta_{ml}\right)\right) \tag{7}$$

where ν_m is the number of cages of type m per water molecule in the hydrate lattice, f_w^β is fugacity of empty hydrate,

$$f_w^\beta(T,P) = P_w^{sat,\beta}(T)\phi_w^{sat,\beta}(T)\exp\left(\frac{\int_{P_w^{sat,\beta}}^{P} V_w^\beta(T,P)dP}{RT}\right) \tag{8}$$

where $P_w^{sat,\beta}$, $\phi_w^{sat,\beta}$, and V_w^β are the saturated vapor pressure, saturated fugacity coefficient, and molar volume of water in the empty lattice, respectively. The θ_{ml} is occupancy (fraction) of each cage type m by a guest l and is given by

$$\theta_{ml} = \frac{C_{ml}\bar{f}_l^V(T,P,y_l)}{1+\sum_l C_{ml}\bar{f}_l^V(T,P,y_l)} \tag{9}$$

where $\bar{f}_l^V$ and y_l are the fugacity and mole fraction of component l in the vapor phase, respectively. It should be noted that the unit cell of a structure I hydrate contains 2 pentagonal dodecahedron