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The application of CPA-vdWP to the phase equilibrium modeling of methane-rich sour natural gas hydrates

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ABSTRACT

To better application of the Cubic-Plus-Association equation of state (CPA-EoS) and van der Waals–Platteeuw (vdW-P) model to the phase equilibrium modeling of the methane-rich sour natural gas, an improved CPA-EoS (iCAP-EoS) with new correlations was proposed. In terms with the new energy parameter *a*, the saturated liquid density of pure component would be described accurately. Additionally, instead of the constant binary interaction parameter, a temperature-dependent binary interaction parameter was developed for calculating the corresponding binary system. As the results shown, the compositions of the fluid phase for the binary mixtures could be performed accurately with the help of the temperature-dependent binary interaction parameter. The predicted results of the proposed model, for both ternary systems and quaternary systems, were compared with the experimental data on the gas hydrate equilibrium dissociation pressures in good agreements with an AAD approximately to 2.28%. Additionally the results shown that the iCPA-vdWP model had an superior accuracy than the original CPA-EoS and vdW-P(CPA-vdWP) model. In high-acidic gas system, the presented model is also within the acceptable errors. Besides the potential application for phase equilibrium model in sour-gas hydrate based separation process is also obtained.

1. Introduction

Sour natural gases, with acidic gases (i.e. hydrogen sulfide and carbon dioxide) concentration more than 5%, which have attracted much attention of society to satisfy the increasing global demand for energy, are generally in equilibrium with gas hydrates at low temperature and/or high pressure reservoir conditions [1]. In addition, in the process of sour natural gas production, transporting and processing, gas hydrates would also be formed owing to the mixture of enough water and gas at certain temperature and pressure, resulting in the plugging of pipeline and instruments. However, methane hydrate is also regarded as a promising alternative energy carrier, with pollution-free, high-efficiency and environmental-friendly characters [2]. Developing an accurate and robust phase equilibrium model for predicting the phase behavior of gas hydrates would be crucial to develop mitigation techniques of managing the gas hydrates formation and making better use of the future energy.

It should be noted that the existence of acidic gases in natural gas contribute to the formation of gas hydrates at relatively higher temperatures and lower pressures [3]. In addition, due to the toxicity of H_2S and the corrosion of acidic gases, measuring thermodynamic behavior of sour natural gas in equilibrium with gas hydrates is not an easy task at current technology [4]. To avoid the disadvantage of the scarce experimental data, developing an accurate thermodynamic model to describe phase equilibria of gas hydrates regarding sour natural gas system is extremely important.

The available thermodynamic models for sour natural gas hydrates were always developed by equating the chemical potential or fugacity of water in all present phases [4]. In addition, since the phase behavior of water in fluid phase is always regarded as the key parameter in the solid hydrate phase model, it is extremely essential to make an accurate description of the fluid phase behavior. As the existence of water and the effect of hydrogen bonding in the fluid phase wouldn't be ignored, several models utilized to describe the effect of hydrogen bonding were proposed, such as Cubic-Plus-Association equation of state (CPA-EoS) [5], PR-Henry approach [6], Perturbed Hard Sphere Chain equation of state (PHSC-EoS) [7,8], Elliott–Suresh–Donohue Equation of State (ESD-EoS) [9,10] and PC-SAFT method [11] etc. The CPA-EoS is the most

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popular method, owing to its simplicity, convenient and high accuracy. Especially, as the studies reported by Ioannis Tsivintzelis et al. [12,13] and Farshad Tabasinejad et al. [14] the CPA-EoS could obtain a satisfied accuracy when utilized to represent the phase equilibria of gas mixture containing CO_2 and H_2S. Whereas, the accuracy of CPA-EoS will be reduced with inappropriate association scheme of components or inaccurate binary interaction parameter [15].

To explain the solid state phase behavior of hydrate systems, Chen and Guo [16] as well as van der Waals and Platteeuw [17] implemented two basic models, respectively. ZareNezhad et al. [18,19] had done a series of studies associated with modeling the phase behaviors of sour natural gas hydrate system based on the Chen and Guo's work, unfortunately the accuracy was decreased with the existence of H_2S and/or CO_2.

The vdW-P model was based on the statistical thermodynamic model, and with the work of Parrish and Prausnitz [20], it was extended to predict hydrate formation conditions for single and multicomponent gas in water. Antonin Chapoy et al. [21] developed different models for the description of fluid phase behavior by revising vdW-P model, and accounted for good results on describing the phase equilibria of gas hydrates. Peter Jorgensen Herslund et al. [22] had implemented and validated a phase equilibrium model of gas hydrates for CO_2 capture based on the CPA-EoS and vdW-P model. With the re-calculated binary interaction parameter and Langmuir adsorption coefficient, the model could describe the phase equilibria of gas hydrate containing CO_2 with high accuracy. Therefore, vdW-P model may have significantly potential applications for the description of the phase equilibria of sour natural gas hydrate system containing acidic gases.

In this work, the authors concentrated on developing a thermodynamic model using CPA-EoS combining with the vdW-P model to applicate it in predicting phase equilibria of sour natural gas hydrate systems in the existence of CO_2 and H_2S. As the essential of performing the phase behavior of fluid phase accurately and the report related to increasing the accuracy of CPA-EoS in describing the phase behavior of sour natural gas was still scared, this work mainly focused on developing an improved CPA-EoS with a new correlation for energy parameter and a temperature-dependent binary interaction parameter. To prove the accuracy of this modified model, this work also validated the predicted dissociation pressure of CPA-vdWP and iCPA-vdWP against experimental data available in the literatures. As the composition of sour natural gas is varied from different gas fields and the common and principal component of hydrocarbon gas within this system was methane, this work only studied the methane-rich sour natural gas. When referring to the complex containing C_2^+, this proposed model may be completed by fitting the corresponding parameters.

2. Phase equilibrium model

Prediction of phase equilibria of sour natural gas in equilibrium with gas hydrates highlights its importance in preliminary study. In this work, a general phase equilibrium model depending on the equality of the fugacity of water in different phases had been used to model the equilibrium conditions of this system.

$$f_w^i = f_w^j \tag{1}$$

where the f_w^i and f_w^j is the fugacity of water in the different phases in equilibria, respectively.

2.1. Improved Cubic-Plus-Association equation of state (iCPA-EoS)

To complete the phase equilibrium model, the iCPA-EoS, combined with the well-known Soave–Redlich–Kwong (SRK) EoS for the physical part and an association term similar to the SAFT model, had been applied to determine water fugacity in fluid phase. Additionally, the iCPA-EoS in terms of pressure P is expressed by Kontogeorgis et al. [23,24] as follows

$$P = \frac{RT}{V_\mathrm{m} - b} - \frac{a}{V_\mathrm{m}(V_\mathrm{m} + b)} - \frac{RT}{2V_\mathrm{m}}\left[1 + \frac{1}{V_\mathrm{m}} \times \frac{\partial \ln g(1/V_\mathrm{m})}{\partial(1/V_\mathrm{m})}\right] \times \sum_i x_i \sum_{A_i}(1 - X_{A_i}) \tag{2}$$

where a denotes the temperature dependent SRK energy parameter, b refers to the temperature independent SRK co-volume parameter and V_m is the molar volume. X_{A_i} rigorously defined as following denotes the mole fraction of molecule i not bonded to the site A and x_i is the mole fraction of component i [25]. where T, P and R are temperature in Kelvin, pressure in MPa and the universal gas constant equaling to 8.314 $\mathrm{m^3\ Pa\ mol^{-1}\ K^{-1}}$, respectively.

$$X_{A_i} = 1 \Bigg/ \left(1 + V_m^{-1} \times \Delta^{A_iB_j} \times \sum_j x_j \sum_{B_i} X_{B_i}\right) \tag{3}$$

where the association strength between site A on molecule i and site B on molecule j, $\Delta^{A_iB_j}$, is the key quantity of CPA-EoS for the associating components and may be defined as

$$\Delta^{A_iB_j} = g(1/V_m) \times \left[\exp\left(\varepsilon^{A_iB_j} \big/ (RT)\right) - 1\right] \times b_{ij}\beta^{A_iB_j} \tag{4}$$

where the radial distribution function, $g(1/V_m)$, may be calculated through Eq. (5). $\beta^{A_iB_j}$ and $\varepsilon^{A_iB_j}$ are the association volume and energy parameters of CPA-EoS, respectively.

$$g(1/V_m) = \left(64V_m^3 - 8V_m^2 b\right) \Big/ (4V_m - b)^3 \tag{5}$$

For pure component the parameters of iCPA-EoS were listed in Table 1. In this work, water was regarded as an associating component and modeled by 4C association scheme which involved two proton donors and two proton acceptors. In addition, according to the report of Tsivintzelis. et al. [13], for mixtures with water and hydrocarbons, a better result would be obtained when H_2S was regarded as self-associating molecule using the 3B association scheme and CO_2 was assumed as solvation with only one proton

Table 1
Pure component for the iCPA-EoS.

	Association scheme	b $10^5/(\mathrm{m^3\ mol^{-1}})$	β	$\varepsilon/(\mathrm{Pa\ m^3\ mol^{-1}})$	Reference
H_2O	4C	1.451	0.0692	16,655	[27]
H_2S	3B	2.895	0.2329	3781	[28]
CO_2	Solvation	2.72	0.1836	8327.5	[19]
		$T_c/(\mathrm{K})$	$P_c/(\mathrm{MPa})$	ω	
CH_4	Non-associating	190.56	4.599	0.0115	[26]