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Application of PHSC equation of state in prediction of gas hydrate formation condition

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ABSTRACT

In this work the modified perturbed hard sphere chain equation of state (PHSC), coupled with Van der waals Platteuw model, has been used for prediction of gas hydrate formation (dissociation) conditions. The PHSC EOS has been modified using association and electrostatic contributions. In order to evaluate the capability of the PHSC EOS, the hydrate formation conditions of various pure as well as mixed gases in the presence and absence of the thermodynamic inhibitors such as methanol, ethanol, mono ethylene glycol(MEG), NaCl, KCl and $CaCl_2$ have been studied. In the absence of inhibitors, the pure gas hydrate formation conditions have been predicted within 3.4% absolute average relative deviation. The hydrate formation condition of gas mixtures have been predicted within AARD 4.6%. In the presence of organic inhibitors and single electrolyte 6.1% and 5.8% AARD has been observed respectively. A total of 102 systems have been studied; our results showed that the PHSC EOS is capable of prediction of hydrate formation condition with reasonable absolute average relative deviation (AARD) from experimental data.

1. Introduction

Water molecules have been known to form clathrate hydrates when stabilized by gas molecules occupying cavities in the crystal. Several hydrate structures have been known (I, II, H). Depends on the size of the guest molecule most non polar and some weakly polar gases form hydrate structures I or II [1]. Methane, ethane, carbon dioxide as well as nitrogen form structure I, while propane and iso-butane forms structure II.

During recent years a lot of researches have been focused on the applications of gas hydrates. It has been suggested for gas transportation [2–4], sweetening of water, wastewater treatment [5], refrigeration and air conditioning systems [6,7], purification of gas mixtures [8–10] and even green house gases capturing [11].

Englezos [12] presented a complete review on technological aspects of natural gas hydrate. In another work Englezos and Lee [13] published a review on available methane hydrate resources in the world. Chatti et al. [14] published a review on the area of interest of gas hydrate. Eslamimanesh et al. [15] done a complete review dealing with experimental studies on application of gas hydrate formation in separation processes in literature.

In contrast, in gas processing plants as well as gas pipelines, hydrate formation condition should be predicted and consequently prohibited, for this purpose thermodynamic or kinetic inhibitors may be used. Thermodynamic inhibitors produce hydrogen-bonded network with water molecules through their hydroxyl groups [16] and, as a result, make the hydrate formation conditions impossible. Traditional polar inhibitors (e.g. methanol, ethanol, ethylene glycol, salt) are still widely used in industrial practices. Considering above facts, prediction of hydrate formation condition is of interest. Firstly, Van der Waals and Platteeuw [17] developed the basic statistical theory for this purpose. Then Parrish and Prausnitz [18] generalized their method. Ng and Robinson [19] as well as Holder et al. [20] improved and expanded the range of applicability of the model. Hammerschmidt [21] developed the first applicable method to predict the effects of inhibitors on the hydrate formation conditions. Anderson and Prausnitz [22] developed a method based on the equality of fugacities. Englezos et al. [23] take the advantages of using Trebble–Bishnoi [24] equation of state and presented a methodology to calculate the inhibition effects of methanol. Jiang and Adidharma [25] used a new version of SAFT EOS to predict the hydrate formation conditions of pure and binary alkanes. Mohammadi and Richon [26] predicted the inhibition effect of ethylene glycol on methane hydrate, using a modified Patel–Teja EOS (VPT-EOS). Tavasoli et al. [27] used Elliot, Suresh and Donohue (ESD) EOS to investigate the hydrate formation in the absence and presence of inhibitors. Zou et al. [28] used Zou–Stenby model for evaluation of inhibition effect of methanol. Chapoy et al. [29] employed CPA EOS for prediction of gas hydrate formation conditions of pure gases. Ma et al. [30] combined Patel–Teja EOS with Gou–Chen Model and predicted hydrate formation conditions in the presence of inhibitors. Eslamimanesh et al. [31] extended the conventional

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Clapyron equation and calculated Pressure–Temperature diagram of carbon dioxide and hydrogen sulfide hydrate. Anderson [32] calculated enthalpies of the reactions utilizing the Clapeyron equation.

In the presence of inhibitor and water, self association as well as cross association between constituents should be taken into account. Li et al. [33], Kontogeorgis et al. [34] and Tavasoli et al. [27] considered this effect using SAFT, CPA and ESD EOSs respectively. On other hand in the presence of electrolytes the phase behavior affected by electrostatic interactions. To consider the long range interactions, usually Debye–Huckel electrostatic term is added to the conventional EOSs. Mohammadi and Richon [35] utilized the modified Aasberg–Peterson model [36] to predict the solubility and inhibition effects of salts. Liao et al. [37] used the modified Zou–Gommesen–Gou EOS [38] to predict the hydrate formation conditions in the presence of methanol, single electrolytes and mixed electrolytes. Haghighi et al. [39] applied CPA EOS to predict hydrate formation condition of methane in the presence of electrolytes with high accuracy. Zou and Stenby [40] modified the extended Patel–Taja to describe the non-ideality of liquid phase containing water and electrolytes.

In this work PHSC EOS has been modified and coupled with Van der Waals and Platteuw model. Gas hydrate formation conditions have been predicted in the absence and the presence of organic inhibitors (methanol, ethanol, MEG) and salts (KCl, NaCl, $CaCl_2$). In the presence of electrolytes primitive MSA has been coupled with PHSC EOS. Thermodynamic framework of this research has been presented in Section 2. In Section 3, the method of parameter estimation has been explained, finally, the results and discussions have been drawn.

2. Thermodynamic framework

The chemical potential equality is the basis of prediction of gas hydrate formation conditions. In equilibrium we have:

$$\mu_w^H = \mu_w^\alpha \tag{1}$$

where μ_w^H is the chemical potential of water in hydrate phase and μ_w^α is the chemical potential of water in any other coexisting phases. In this work, equilibrium conditions between hydrate (H), aqueous (L) and vapor (V) phases are predicted. Chemical potential of the component in hydrate phase is obtained using the van der Waals and Platteuw model [17]. Following assumptions have been considered in their model: 1 – each cavity contains at most one gas molecule, 2 – there is no interaction between encaged molecules, 3 – the ideal gas partition is applicable to the guest molecules. Considering mentioned assumptions the chemical potential of water in the filled hydrate lattice is expressed by the following equation:

$$\mu_w^H(P,T) = \mu_w^\beta + RT\sum_i^N \lambda_i Ln\left(1 - \frac{C_{ki}f}{1+\sum\limits_{ki} C_{ki}f_k}\right) \tag{2}$$

where μ_w^β is the chemical potential of water in empty lattice f_k is the fugacity of the component i in the gas phase, λ_i is the number of cavities of type i per water molecule in the lattice and C_{ki} is the Langmuir constant [41].

The fugacity of the gaseous compound i can be calculated using an equation of state. (EOS):

$$f_i^v(P,T,y) = \phi_m(P,T,y,EOS) \times P \times y_i \tag{3}$$

Using Lennard–Jones–Devonshire cell theory, the Langmuir constant is expressed as:

$$C_{(T)} = \frac{4\Pi}{KT}\int_\circ^\infty \exp\left[\frac{-w(r)}{KT}\right] r^2 dr \tag{4}$$

where $w(r)$ is the spherically symmetric cell potential and k is the Boltzmann's constant. Parrish and Prausnitz applied the first modification by taking into account multiple guests in the hydrate structures. They used Kihara potential with spherical core and described the guest–host interactions, therefore the cell potential defined as follows:

$$w(r) = 2z\varepsilon\left[\frac{\delta^{12}}{R^{11}r}\left(\delta^{10} + \frac{a}{R}\delta^{11}\right) - \frac{\sigma^6}{R^5 r}\left(\delta^4 + \frac{a}{R}\delta^5\right)\right] \tag{5}$$

$$\delta^N = \left[\frac{(1-(r/R)-(a/R)^{-N} - (1-(r/R)-(a/R))^{-N}}{N}\right] \tag{6}$$

r is the cell radius of the cavity, z is the coordination number, a is the core radius, ε is the characteristic energy and $\sigma+2a$ is the collision diameter. The water chemical potential in β phase (liquid or ice) is defined as follows:

$$\mu_w^\alpha(P,T) = \mu_w^\circ(P,T) + RTLna_w \tag{7}$$

where μ_ω° is the chemical potential of pure water (as ice or liquid), a_w is the activity of pure water as ice or liquid. In equilibrium quality of chemical potentials will satisfy as follows:

$$\Delta\mu_w^\alpha(P,T) = \mu_w^\alpha(P,T) - \mu_w^\beta(P,T) \tag{8}$$

$$\Delta\mu_w^H(P,T) = \mu_w^H(P,T) - \mu_w^\beta(P,T) \tag{9}$$

consequently:

$$\Delta\mu_w^\alpha(P,T) = \Delta\mu_w^H(P,T) \tag{10}$$

Parrish and Prausnitz [18] proposed Eq. (11) for calculation of Langmuir constants. Tavasoli et al. [27] compared this correlation with theoretical values of Langmuir constant and showed that it can be used efficiently. In this work we use this correlation as well.

$$C_{mj} = \frac{A_{mj}}{T}\exp\left(\frac{B_{mj}}{T}\right) \tag{11}$$

From classical thermodynamics Eq. (12) will derive:

$$\frac{\Delta\mu_w^\alpha}{RT} = \frac{\Delta\mu_w^{\circ\alpha}}{RT_\circ} - \int_{T_\circ}^{T}\frac{\Delta H_w^\alpha}{RT^2}dT + \int_{P_\circ}^{P}\frac{\Delta V^w}{RT}dP - Lna_w \tag{12}$$

where $\Delta\mu_\circ^\omega$ is the difference in the chemical potential of water in the empty lattice and liquid water at $T_0 = 273.15$ K, ΔH_w and ΔV^w are the difference in molar enthalpy and molar volume between the empty lattice and liquid water respectively. The difference of molar enthalpy can be calculated as Eq. (13):

$$\Delta H_w^H = \Delta H_\circ + \Delta C_p(T - T_\circ) \tag{13}$$

ΔH_0 and ΔV^w are considered to be pressure independent [41]. a_w can be calculated using Eq. (14):

$$a_w = \frac{\hat{f}_w^l}{f_w^{purw,L}} = x_W^L\frac{V^{o,l}}{V^l}\exp\left[\frac{\mu_w^{res}(T,V) - \mu_w^{res,o}(T,V)}{KT}\right] \tag{14}$$

In this equation $\hat{f}_w^l$, ${f_w}^{pure}$, x_w^l, $V^{\circ,l}$ and V^l are the fugacity of water in aqueous phase, the fugacity of pure water in liquid phase, mole fraction of water in aqueous phase, the molar volume of liquid pure water and the molar volume of aqueous phase respectively. ${\mu_w}^{res}(T,V)$ is the residual chemical potential of water and ${\mu_w}^{res,0}(T,V)$ is the residual chemical potential of pure water in liquid phase. Cole and Goodwin [42] showed that at the incipient hydrate formation conditions, the amount of hydrate phase is nearly zero and the formed hydrate does not have considerable effect on mass balance of the coexisting phases. Consequently, two phase flash calculation can be applied to obtain hydrate formation pressure in the related temperatures and certain concentrations of inhibitors or electrolytes. In this work we neglect the presence of electrolytes in the vapor phase.