



Evaluation of various types' equations of state for prediction of rate of double gas hydrate formation based on Kashchiev model in flow loop apparatus



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ARTICLE INFO

Article history:

Received 30 December 2013

Received in revised form

10 March 2014

Accepted 11 March 2014

Available online 18 April 2014

Keywords:

Gas consumption rate

Kinetic hydrate inhibitors

Equation of state

Kashchiev model

Gaseous mixture

Mini flow loop apparatus

ABSTRACT

This paper compares the effects of using various types of equations of state such as Peng Robinson (PR), Soave Redlich Kwong (SRK), Esmailzadeh – Roshanfeker (ER), Patel Teja (PT) and Valderrama–Patel–Teja (VPT) on the rate of hydrate formation based on the Kashchiev model for gaseous mixtures with experimental data points obtained in a mini flow loop apparatus in presence of the kinetic inhibitors (such as modified starch and L-tyrosine) at various pressures (1–4 MPa) and specified temperature (277.15 K). For this purpose, a laboratory mini flow loop apparatus was set up to measure the rate of gas hydrate formation when a hydrate forming mixture is contacted with water in the presence or absence of dissolved inhibitor under suitable temperature and pressure conditions. In each experiment, a water blend saturated with pure gas is circulated up to a required pressure. Pressure is maintained at a constant value during experimental runs by means of the required gas make-up. The total average absolute deviation was found to be 18.7%, 19.8%, 19.2%, 20.2% and 20.7% of the PR, ER, SRK, VPT and PT equations of state for calculating of gas consumption for gaseous mixtures during gas hydrate formation (in the presence and absence of kinetic gas hydrate inhibitor), respectively. Comparison results between the calculated and experimental data points of gas consumption were obtained in a flow loop indicate that the PR and ER equations of state have lower errors than the SRK, VPT and PT equations of state for this model.

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1. Introduction

Gas hydrates are crystalline clathrate compounds of gas molecules in water, which form under specific temperature and pressure conditions. Clathrates are cage structures formed between a host molecule and a guest molecule. A hydrocarbon hydrate generally is composed of crystals formed by water host molecules surrounding the hydrocarbon guest molecules. (Klug and Feustel, 2003). Gas hydrates are reviewed in-depth by Sloan (1998). Natural gas hydrates are a nuisance in the production, transportation and processing of natural gases. There are two broad techniques to overcome or control the hydrocarbon hydrate problems, namely thermodynamic and kinetic. From the thermodynamic approach, there are a number of reported or attempted methods, including water removal, increasing temperature, decreasing pressure, the addition of “antifreeze” to the fluid and/or a combination of these. The kinetic approach generally attempts (a) to prevent the smaller

hydrocarbon hydrate crystals from agglomerating into larger ones (known in the industry as an anti-agglomerate and abbreviated AA) and/or; (b) to inhibit and/or retard initial hydrocarbon hydrate crystal nucleation; and/or crystal growth. Thermodynamic and kinetic hydrate control methods may be used in conjunction. The kinetic inhibitors are commonly labeled Low Dosage Hydrate Inhibitors (LDHI) in the literatures. Kinetic inhibition is a recently proposed alternative to thermodynamic inhibition (Sloan, 1998). Various models have been published on the basis of the crystallization theory for the prediction of gas hydrate formation. One of the most important parameters in these models is driving force. In order to calculate the driving force of hydrate formation corresponding thermodynamic models are required for the calculation of fugacity of different components in the gas phase at equilibrium and experimental conditions. For example, Gnanendran and Amin (2004) used the SRK equation of state to determine the gas phase properties. Sloan (1998) used the SRK equation of state for the calculation of the driving force and the prediction of hydrate equilibrium pressure. The results indicate that the SRK equation of state treats the equilibrium pressure well in comparison with the

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experimental data. Kashchiev and Firoozabadi (2002a,b) used the PR equation of state for the prediction of the induction time and the gas consumption rate by using the calculation of the driving force. They found that the sharp decrease in the induction time, with increasing super-saturation, is largely due to the strong super-saturation dependence of the rate of hydrate nucleation. Englezos and Bishnoi (1988) used the PR equation of state for the calculation of the driving force by using the fugacity coefficient of the components in the gas phase resulting in the proposed model's capability to describe the experimental data quite well with a prediction error of less than 11.3%. In addition, at higher driving forces, the rate of gas consumption is higher.

In this work, an approach for the prediction of the gas consumption rate for multi-component gas hydrate formation based on the Kashchiev model (2000) is developed from the correlations of simple gas hydrate formation using the calculation of the gas mole fraction in hydrate phase and the prediction of the hydrate formation rate for each guest component in gaseous mixture. In addition, in the proposed model, the effect of using two parametric equations of state, the SRK (Soave, 1972) and PR (Robinson and Peng, 1976) and three parametric equations of state, the ER (Esmaeilzadeh and Roshanfekr, 2006), PT (Patel and Teja, 1982) and VPT (Valderrama, 2003) for the prediction of the gas consumption rate by means of calculating the driving force from the fugacity coefficient of the components in the gas phase is investigated.

2. Rate of hydrate formation

Hydrate nucleation is a microscopic process, during which small hydrate crystals (nuclei) grow and disperse in an attempt to achieve critical nuclei size for continued growth (Sloan, 1998). The presence of non-polar molecules, such as hydrocarbons, in water, distorts the water molecules inducing them to 'arrange' themselves into clusters (nuclei). These clusters increase in number through a process of continuous fading and growing to a critical size before rapid hydrate growth proceeds. Gas hydrate formation is a complex multiphase crystallization process. As such, it is difficult to observe experimentally and various approaches have been followed to monitor the hydrate formation and decomposition at different levels of detail (Sloan, 2003a, 2003b). The time taken for nucleation is referred to as the induction time. The hydrate nucleation process in practical situations is a heterogeneous nucleation process, as homogeneity is rarely achieved. Morphology studies involve observations of hydrate formation at fluid/fluid interfaces and offer valuable information on the mechanistic aspects of crystal nucleation, growth, and decomposition. These studies complement traditional gas uptake measurements, structural investigations and molecular simulations (Englezos et al., 1987a). Hydrate formation occurs at the water–gas interface, as the gas is present at its higher concentration in the interface, more so than in the bulk liquid. The interface also lowers the Gibbs-free energy which is conducive for hydrate nucleation. Englezos et al., (1987a, 1987b) developed a mechanistic model based on crystallization kinetics and mass transfer effects to predict the hydrate formation kinetics of methane and ethane hydrates in a constant pressure stirred-tank gas–water system. Later the model was simplified by Skovborg and Rasmussen (1994) to a mass transfer limited model for multi-component gas mixtures. Bourgmayer et al., (1989) measured the formation rate of methane and ethane mixtures in a semi-batch reactor in the presence of a condensate. Kashchiev and Firoozabadi (2002a,b, 2003) published a comprehensive study on hydrate nucleation and growth kinetics based on classical nucleation and crystallization principles for single component gas hydrate systems. The work also quantified the effects of additives in the formation of hydrates when present in water, and distinguished

how certain additives acted as hydrate promoters while others acted as hydrate kinetic inhibitors. The Kashchiev and Firoozabadi model was developed based on a single gas component system. In the following sections, rate of gas consumption for gaseous mixtures during gas hydrate formation in mini flow loop apparatus was described.

2.1. Hydrate formation based on equilibrium thermodynamics

The hydrate formation equilibrium of water–multicomponent gas system can be predicted from a statistical thermodynamic model. Based on the proposed thermodynamic model for the hydrate three-phase equilibrium, an equilibrium hydrate formation gas to water ratio can be calculated at (P_{eq}, T_{exp}) using the cavity fractional filling calculation in the hydrate. The fractional filling of cavities was founded based on a Langmuir adsorption isotherm (Bourgmayer et al., 1989). The fractional filling of component k in cavity type j ($j = 1, 2$ for hydrate structures sI and sII) is given as:

$$\theta_{k,j} = \frac{C_{k,j} f_k^{eq}}{1 + \sum_{k=1}^m C_{k,j} f_k^{eq}} \quad (1)$$

Where, f_k^{eq} is the fugacity of component k at equilibrium condition, $C_{k,j}$ is the Langmuir adsorption constant is calculated by Equations 5–22 in the ref. (Sloan, 1998). Therefore, the total numbers of gas components k per water molecule in hydrate structures sI and sII is given as

$$N_k = \nu_1 \theta_{k,1} + \nu_2 \theta_{k,2} \quad (2)$$

Where ν is the number of cavities per water molecule (for example $\nu_1 = 2/17$ and $\nu_2 = 1/17$ for structure II hydrates). Therefore, on a molar basis, the total moles of gas in hydrates per mole of water could be calculated as:

$$\beta = \sum_{k=1}^m N_k \quad (3)$$

The composition of the hydrate could also be calculated as:

$$\text{For gas components : } x_k^g = \frac{N_k}{1 + \sum_{k=1}^m N_k} \quad (4)$$

$$\text{For water : } x_w = \frac{1}{1 + \sum_{k=1}^m N_k} \quad (5)$$

2.2. Supersaturation for gaseous mixtures during gas hydrate formation

Several driving forces have been used in modeling of the hydrate formation kinetics, and those most frequently used in experimental studies are related to the hydrate equilibrium curve. Vysniauskas and Bishnoi (1983) used sub-cooling as the driving force for nucleation and growth. Sub-cooling is defined as the difference between the hydrate equilibrium temperature at the experimental pressure and the experimental temperature. Sub-cooling is easily determined by measuring the experimental temperature and calculating the hydrate equilibrium temperature using a thermodynamic model. Englezos et al., (1987a, 1987b) used the difference

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