Modeling of Methane Hydrate Inhibition in the Presence of Green Solvent for Offshore Oil and Gas Pipeline

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ABSTRACT

In offshore gas transmission pipeline systems, typically gas and water are produced under high pressure and low temperature conditions causing the formation of gas hydrates blocking pipelines. Thermodynamic modeling is necessary to understand the phase stability of hydrate in the presence of green solvents namely, ionic liquids (ILs). In this work, the thermodynamic models are based on the computation of fugacity of hydrate phase using Van der Waals and Platteeuw solid solution theory combined with Peng – Robinson equation of state (PR-EoS) for fugacity of hydrate former in the gas phase and the computation of fugacity of aqueous water phase using activity coefficient models such as the non – random two – liquid (NRTL) model and Pitzer – Mayorga model. The model results are compared with available experimental data from open literature and observed to be in good agreement with the reported literature. Finally, the hydrate suppression temperature due to ILs on methane hydrate is calculated to know the inhibition effectiveness of IL on methane hydrate formation in offshore pipeline system. The overall accuracy of Pitzer-Mayorga model is found to be 5.8 % while NRTL model’s accuracy was 6.3 % for various ILs and methane hydrate system. Model results further indicated that ILs with shorter alkyl chain length exhibit better inhibition effect. The model developed in this work shows potential application in the determination of hydrate phase stability using green solvent for offshore oil field applications.

KEY WORDS: Gas hydrate; inhibition; ionic liquids; phase equilibrium; thermodynamic model.

INTRODUCTION

Gas hydrate is ice like crystalline structure, which contains the ‘guest’ gas enclosed in a structure formed by the ‘ghost’ water molecule by hydrogen bonding. The most common type of gas hydrates are structure I (sI), structure II (sII) and structure H (sH), where each structure contain definite number of large and small cavities formed by water molecules (Sloan and Koh, 2008). In offshore gas transmission pipeline systems, typically gas and water are produced under high pressure and low temperature conditions causing the formation of gas hydrates which blocks the pipelines (Hammerschmidt, 1934). Currently, four types of methods namely, depressurization, de-watering, heat addition and chemical inhibition are available to prevent gas hydrate formation. As per safety concerns, the most common method to prevent gas hydrates formation is using chemicals such as alcohols, glycols, etc. There are two types of chemical inhibitors: kinetic and thermodynamic inhibitors. The performance of kinetic inhibitors is to delay the nucleation and the crystal growth of gas hydrates. The thermodynamic inhibitors does inhibit the hydrate nucleation, growth and agglomeration of hydrate by shifting hydrate (H) - liquid (L) - vapor (V) phase equilibrium conditions to high pressure or/and low temperature conditions. However, due to environmental concerns, green solvent such as ILs having negligible vapor pressure and high thermal stability are expected to gain importance in hydrate inhibitions. Several investigations have been carried out on methane hydrate inhibition in the presence of IL systems (Sloan and Koh, 2008; Xiao et al., 2010; Li et al., 2011; Kim et al., 2011; Keshavarz et al., 2013; Partoon et al., 2013; Richard and Adidharma, 2013; Zare et al., 2013).

Xiao et al. (2010) studied the effect of imidazolium cation based ILs with different alkyl chain length and anions such as chloride (Cl), bromide (Br), iodide (I) and tetrafluoroborate (BF4) on methane hydrate system. They reported that ILs are capable of performing both as kinetic and thermodynamic inhibitors for methane hydrate formation. The study shows that ILs have strong electrostatic charges and hydrogen bond with water which helps in shift H-L-V phase equilibrium curve to a lower temperatures at given pressure and also delaying hydrate formation by slowing down the hydrate nucleation rate. Kim et al. (2011) hypothesized that screening of ILs for hydrate inhibition must have the two following criteria: 1. The IL must be hydrophilic and 2. Cation