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Inhibition effect of amino acids on carbon dioxide hydrate

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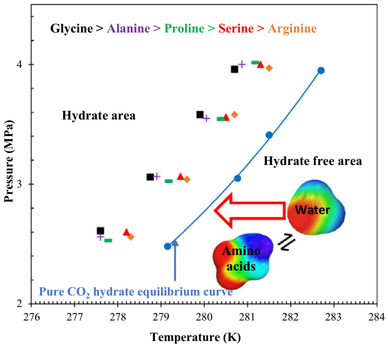
HIGHLIGHTS

- New data on amino acids as CO_2 hydrate thermodynamic inhibitors is reported.
- COSMO-RS is used to study the inhibition impact of amino acids.
- COSMO-RS method for screening amino acids for hydrate inhibition is proposed.
- The CO_2 hydrate phase boundary in the presence of amino acids is modelled.

GRAPHICAL ABSTRACT



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ABSTRACT

The formation of gas hydrates hinders oil & gas transportation in pipelines, however, adequate knowledge and understanding of the gas hydrate phase behaviour is a key to its prevention. Thus, this study reports the inhibition effect of glycine, alanine, proline, serine and arginine on the carbon dioxide hydrate phase equilibrium condition using the isochoric T-cycle method in the pressure range of 2.53–4.0 MPa. The studied amino acids concentrations ranged from 5 to 20 wt%. The presence of all the studied amino acids significantly shifted the carbon dioxide hydrate phase boundary to higher pressures and/or lower temperatures area, hence indicating inhibition effect. Glycine is found to show the highest inhibition strength with an average depression temperature of 1.83 K at 10 wt%. In agreement with COSMO-RS sigma profile analysis, the amino acids inhibitions strengths are found to be influenced by their ability to reduce water activity in hydrate formation via hydrogen bonding with water molecules. The calculated carbon dioxide hydrate dissociation enthalpies in the presence of amino acids, suggested that, amino acids do not take part in carbon dioxide hydrate cage occupation and structure during hydrate formation. Furthermore, the measured carbon dioxide hydrate phase conditions in the presence of amino acids are predicted and are found to be in good agreement with the experimental data.

1. Introduction

Gas hydrate is known as a major challenge to the oil and gas flow assurance, as it causes pipeline blockages (Hammerschmidt, 1934; Xiao and Adidharma, 2009). The formation of gas hydrate in pipeline can lead to operational shutdowns, huge maintenance cost, environmental hazards, and in worst cases, loss of lives. In light of this, carbon dioxides hydrates have gain significant attention since they constitute natural gas composition and are mostly injected into aquifers through pipelines for CO_2 sequestration (Roosta et al., 2016). There are high CO_2 – content natural gas reservoirs around the globe. They are mostly found in the South

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Nomenclature

AAE	average absolute error
T	temperature, K
$T_{f(i)}$	freezing point temperatures of water, 273.15 K
T_f	freezing point temperatures of aqueous amino acid solution, K
P	pressure, MPa
n	hydration number, 6.0
ΔH_d	dissociation enthalpy, kJ/mol
a	activity
Z	compressibility factor
m	number of data points
R	universal gas constant, 8.314 J/(mol·K)
$\Delta H_{FUS(i)}$	heat of fusion of ice, 6008 J/mol

Subscripts

aa	amino acid
w	water
Cal.	calculated
Exp.	experimental

China Sea, Gulf of Thailand, Australian Cooper-Eromanga basin, Taranaki basin, New Zealand and North Sea South Viking Graben. Malaysia is one of major producers and exporters of natural gas in the world with estimated reserve of about 88.0 tscf. Malaysia, Thailand and Indonesia are among countries in the world having gas reservoirs that have over 0.50 mole fraction of CO_2 (Nasir et al., 2014). This high amount of CO_2 alongside the deep-waters temperatures and pressures conditions makes these fields more prone to hydrate formation during exploration and production. Therefore, CO_2 hydrate inhibition methods is relevant for successful offshore operation in such fields.

Currently the injection of chemical inhibitors in pipelines is the most practiced gas hydrate prevention method employed in the industry. Two main kinds of gas hydrate inhibitors are generally used; Thermodynamic gas hydrate inhibitors (THIs) and low dosage gas hydrate inhibitors (LDHIs). THIs such as alcohols (methanol and ethanol) and glycols are used to shift the hydrate equilibrium phase to higher pressures and/or lower temperatures areas (Cha et al., 2013; Koh et al., 2011). Alike anti-freezing agents, the application of conventional THIs demands high concentrations (up to 50 wt%) of these chemicals increasing their volatile content (Broni-Bediako et al., 2017; Lee et al., 2013). Hence, utilization of THIs is environmentally prohibitive and cost intensive. Alternatively, LDHIs are basically polymers and are used to delay hydrate nucleation time (Bavoh et al., 2016a; Kelland, 2006; Perrin et al., 2013). However, their inhibition influence is probabilistic and perform poorly at higher subcooling conditions (Bavoh et al., 2016b; Kelland, 2006; Sloan and Koh, 2007). Notwithstanding, they are still active search for THIs that are effective and environmentally friendly.

Recently, Sa et al. (2011) introduced natural amino acids as novel THIs for carbon dioxide hydrates. They believed, since, amino acids can form hydrogen bonds with water molecules, they can also act as THIs. In addition, they act as zwitterions and can electrostatically interact with water. Most importantly, they are environmental friendly, biodegradable, soluble in water and can be acquired in large quantities at relatively low cost. In their work, the effect of glycine, alanine, and valine on the phase boundary of carbon dioxide hydrate were studied at pressures of 1.41–3.52 MPa and concentration range of 0.1–3 mol% (0.39–11.56 wt %). They found that, amino acids inhibited carbon dioxide hydrate in the order of increasing magnitude; glycine < alanine < valine (based on mol%). Sa et al. (2016) further suggested that, glycine, alanine, serine, and proline can thermodynamically and kinetically inhibit methane and natural gas hydrates (93% CH_4, 5% C_2H_6, 2% C_3H_8). The study was conducted in a concentration range of 1.93–52.67 wt%. A similar trend of hydrate inhibition was observed in in CH_4 and natural gas hydrates, with an order of inhibition of proline > serine > alanine > glycine (on the bases of 1.3 mol%). However, a recent study revealed that the type of concentration unit (mol% or wt%) adopted for hydrate studies significantly affects the trend and interpretation of inhibition (Bavoh et al., 2016c). Mostly the oil and gas industry apply inhibitors on wt% bases, thus it is recommended to use wt% as it gives better hydrate inhibition evaluation that is relevant and related to practical field application. Readers may refer to (Bavoh et al., 2016c; Mech et al., 2015) for more details on the effect of concentration units on gas hydrate inhibition. On the other hand, (Sa et al., 2013) reported that, glycine, alanine, valine, leucine, isoleucine can kinetically inhibit CO_2 hydrates via local water perturbation (Sa et al., 2014). Glycine showed the highest kinetic inhibition impact at 0.1 mol% (0.39 wt %). Amino acids with shorter alkyl side chain were found to perform better than longer ones for kinetics inhibition. They extended their work on the kinetic inhibition effect of l-alanine, aspartic acid, asparagine, phenylalanine, and histidine on CO_2 hydrate nucleation and growth kinetics at 0.01 and 0.1 mol% (0.039–0.39 wt%). It was found that aspartic acid and asparagine demonstrated a high inhibition impact than alanine at 0.01 mol% (0.0039 wt%), however, at 0.1 mol% (0.39 wt%), histidine kinetically showed the highest inhibition impact followed by alanine and phenylalanine (Sa et al., 2015). Glycine and leucine are also known to kinetically inhibit THF (Naeiji et al., 2014), and C_2H_6 hydrates (Rad et al., 2015). However, some amino acids are reported to kinetically promote methane hydrates (Bhattacharjee et al., 2016; Liu et al., 2015; Veluswamy et al., 2016). In addition, most recently Cai et al. (2017) reported some natural amino acid (L -Methionine) as a kinetic CO_2 hydrate promoter. The current reported literature on the effect of amino acids on the thermodynamics of CO_2 hydrate inhibition are focused on glycine, alanine, and valine at moderately high pressures (<3.6 MPa). It is therefore pertinent that further studies to understand the effect of other amino acids on CO_2 hydrates be carried out.

Previously, we studied the thermodynamics inhibition effect of glycine, alanine, proline, serine, and arginine on CH_4 hydrates (Bavoh et al., 2016c). Herein, the study is extended to CO_2 hydrate. The impact of proline, serine, and arginine on CO_2 phase boundary are reported for the first time in this paper. These amino acids are selected as their side chain properties exhibit hydrogen bond affinity for water molecules which is relevant for gas hydrate inhibition. The normal concentration needed to avoid hydrate formation in the industry is 24 wt% (Yousif, 1998). Therefore, the selected amino acids are tested below the general industrial THIs application concentration (up to 20 wt%) to effectively test their thermodynamic inhibition impact. In addition, an attempt is made to predict the hydrate equilibrium curve for carbon dioxide in the presence of the studied amino acids using the Dickens and Quinby-Hunt (1997) model.