

Inhibiting effects of transition metal salts on methane hydrate stability



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HIGHLIGHTS

- Effects of transition metal salts on methane hydrate stability were evaluated.
- Differential Scanning Calorimetry was employed to determine dissociation temperature.
- Hydrate inhibition increases in the order: $\text{FeSO}_4 \approx \text{CuSO}_4 < \text{MnSO}_4 \approx \text{AgNO}_3 \approx \text{CaCl}_2 < \text{NaCl} < \text{FeCl}_3$
- Charge and size of the anion and cation of tested salts appears to explain behavior.

ARTICLE INFO

Article history:

Received 27 March 2016

Received in revised form

5 June 2016

Accepted 12 June 2016

Available online 18 July 2016

Keywords:

Methane hydrate

Differential scanning calorimetry

Inhibitor

Transition metal salt

ABSTRACT

The behavior of clathrate hydrates in the presence of transition metal salts was investigated using a Differential Scanning Calorimeter (DSC). Specifically, a DSC was employed to determine the onset temperature for methane hydrate decomposition in the presence of ferric chloride hexahydrate, $[\text{FeCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$, anhydrous ferric chloride, FeCl_3 , MnSO_4 , FeSO_4 , CuSO_4 , and AgNO_3 , and to compare the inhibiting properties of these transition metal salts with NaCl and CaCl_2 , two well-known salt inhibitors. The degree of methane hydrate inhibition induced by the salts that were studied (as indicated by the reduction in dissociation temperature at a given pressure), when compared between mixtures with the same mole percentages of the salt, increases in the following order: $\text{FeSO}_4 \approx \text{CuSO}_4 < \text{MnSO}_4 \approx \text{AgNO}_3 \approx \text{CaCl}_2 < \text{NaCl} < \text{FeCl}_3$. A smaller decrease in the dissociation temperature was observed with salts that contained the larger sulfate anion when compared to salts that contained the smaller chloride anion. Smaller decreases in the dissociation temperature were observed with salts that contained smaller cations like Fe^{2+} when compared to salts that contained larger cations such as Ag^+ and Mn^{2+} . It is posited that the interaction between water with salt ions results in hydrate formation inhibition and the strength of the salt ion-dipole bond between the metal ion and water molecules correlates with the degree of inhibition. Consideration of the charge and size characteristics of the anion and cation components of the tested salts appears to explain this behavior.

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1. Introduction

Clathrate hydrates are crystalline compounds consisting of polyhedral cavities formed from networks of hydrogen-bonded water molecules, in which suitable guest molecules reside (Sloan and Koh, 2008). Natural gas hydrates (clathrate hydrates formed from water and low molecular weight alkanes—primarily methane, CH_4) were identified as the source of plugging in oil and gas pipelines in the 1930s. This discovery launched a major effort to develop solutions to the problem, which marked the beginning of the modern research era for clathrate hydrates (Sloan and Koh, 2008).

Formation of clathrate hydrates can be prevented using thermodynamic inhibitors such as alcohols and salts. These inhibitors

shift the equilibrium between the three phases, hydrate (H), liquid water (Lw), and guest molecular vapor (V) to lower temperature or higher pressure (Sloan and Koh, 2008). It has been posited that dissolved inhibitors tie up water molecules needed for hydrate formation via hydrogen bonding, as in the case of alcohols and glycols (Nihous et al., 2009), or via Coulombic forces, as in the case of salt ions (Sloan and Koh 2008).

Alcohols are frequently employed by the oil industry to avoid hydrate blockages in natural gas pipelines since the potential for undesirable side reactions (such as corrosion) is low relative to salts; however, amounts needed may reach 50 wt% (aq), leading to high costs and disposal problems (Kelland, 1994; Dholabhai et al., 1997). In addition to alcohols and salts, other inhibitors include kinetic inhibitors, like polyvinyl caprolactam (PVCap) or polyvinylpyrrolidone (PVP) and ionic liquids, e.g., dialkylimidazolium halide compounds, which have been studied more recently (Sloan

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et al., 1996; Xiao and Adidharma, 2009). Kinetic inhibitors are quite effective in delaying the crystallization of gas hydrates (Sloan et al., 1996), whereas ionic liquids exhibit both thermodynamic and kinetic inhibition features (Xiao and Adidharma, 2009).

Studies have been conducted to investigate the roles played by cations and anions in the inhibition of hydrate formation (Lu et al., 2001; Sabil et al., 2010). Lu et al. (2001) compared the effects of salts with different cations and anions on hydrate phase equilibria of CO₂, CH₄, and C₃H₈ hydrates. In particular, they compared CH₃CO₂Na versus CH₃CO₂H at different concentrations and found that the stability of CO₂ hydrate was affected by the concentration of CH₃CO₂⁻ and CH₃CO₂H but not Na⁺. In addition, it was observed that there was a larger shift in the equilibrium temperature of methane hydrate with MgSO₄ versus MgCl₂, but not a very large difference between NaCl versus KCl and CaCl₂. They concluded that the anion has a greater influence on hydrate stability than the cation, and posited that difference was due to interactions between liquid water molecules and ions.

In electrolyte solutions, hydrate formation may be hindered by disruption of the ambient water network that is driven by hydrogen bonding. Lu et al. (2001) argued that, based on studies performed by Mizuno et al. (1997) on hydrogen bonds in aqueous solution of halogenated alcohols, anions exert a greater influence on hydrogen bonding of water molecules than cations and are, therefore, more important in inhibiting hydrate crystallization.

Sabil et al. (2010) compared the effects of salts with different cations and anions on hydrate phase equilibria of mixed CO₂/THF hydrates using a Cailletet apparatus. Their observations did not support the assertion by Lu et al. (2001) that anions are more important than cations in suppressing hydrate formation. They found that the inhibiting effect increased in the following order: NaF < KBr < NaCl < NaBr < CaCl₂ < MgCl₂, and concluded that the inhibition of the hydrate increased with the charge of the cation, and the radius of the anion. They proposed that this trend was the result of the strength of the ion-hydrogen bonds which either disrupts or reinforces the ambient water networks. The authors noted that the electrolyte concentrations that were investigated (0.5 and 1 mol%) were relatively low and that higher concentrations might yield different results.

The mechanism underlying the influence of salts on hydrate stability has not been clearly identified and warrants additional study, insofar as this has relevance to a host of engineering and scientific issues including the development of new reagents for flow assurance in natural gas pipelines and the formation and dissociation of hydrates in the seafloor and in permafrost. It is important to understand this mechanism since methane recovery and transport from marine hydrates or conventional reservoirs can take place in an ocean environment that contains these types of salts. According to Barnes (1954), and more recently, Millero et al. (2008), the top five ions present in seawater with the highest molality (moles/kg of solvent) are Cl⁻, Na⁺, Mg²⁺, SO₄²⁻, and Ca²⁺. Transition metals, such as iron, manganese, copper, cobalt and nickel, are also commonly found in seawater at trace concentrations. The source and biogeochemical processes related to these elements are still not well understood (Aparicio-Gonzalez et al., 2012).

Other studies of the effects of metals on methane hydrate formation have been conducted, although these studies focused on the elemental forms of the metal. Fan et al. (2012) examined the effect of aluminum foam along with sodium dodecyl sulfate on methane hydrate formation. They concluded that aluminum foam accelerated formation of methane hydrate by promoting hydrate nucleation and enhancing heat transfer. Unlike salts, elemental aluminum does not dissolve in the water phase.

In the present investigation, we conducted experiments to determine the effects of some transition metal salts and other salts

on the behavior of clathrate hydrates decomposition using a Differential Scanning Calorimeter (DSC). Specifically, a DSC was employed to determine the onset temperature for methane hydrate decomposition in the presence of ferric chloride hexahydrate, [FeCl₂(H₂O)₆]Cl·2H₂O (Lind, 1967), anhydrous ferric chloride, FeCl₃, MnSO₄, FeSO₄, CuSO₄, and AgNO₃ and to compare the inhibiting properties of these transition metal salts with NaCl and CaCl₂, two well-known salt inhibitors. These transition metal salts were chosen because they are soluble in water and each transition metal represents metals with varying charges (+1, +2, +3), which are commonly found in the ocean. We attempted to determine whether the inhibiting properties of these salts on methane hydrates follow the trends observed by Sabil et al. (2010).

Decomposition temperature was studied rather than formation temperature since the formation of non-stoichiometric gas hydrates may be influenced by a host of factors such as nucleation, diffusion, and history, which can result in various levels of sub-cooling when using the DSC (Sloan and Koh 2008). This complicates identifying a formation temperature. If, however, care is taken to form pure phases of hydrates with fixed compositions, then decomposition processes may be investigated using DSC, and the measured dissociation temperature can be correlated to the temperature of hydrate formation of those fixed compositional phases.

DSC is commonly used to determine two-phase equilibrium data; however, the application of DSC to study hydrate phenomena has only occurred recently. DSC has been successfully employed to investigate equilibrium phase transitions, dissociation enthalpies and heat capacities of various gas hydrates (Kharrat and Dalmazzone, 2003; Jager et al., 2002; Gupta et al., 2008; Lafond et al., 2012).

2. Experimental materials and methods

Shown in Fig. 1 is a schematic diagram of the system used to perform the experiments. The primary component of the system is a TA Instruments Multi-Cell μ DSC. This DSC has the capability of testing three samples simultaneously and has a detection limit of 0.2 μ W over an operating temperature range of about 233 K to 433 K (-40.0 °C to 160.0 °C) and pressures up to 40 MPa. The Hastelloy sample cells have a volume of 0.5 ml.

The sample cells are pressurized through capillary tubing attached to the cell closures. The capillary tubing is connected to the

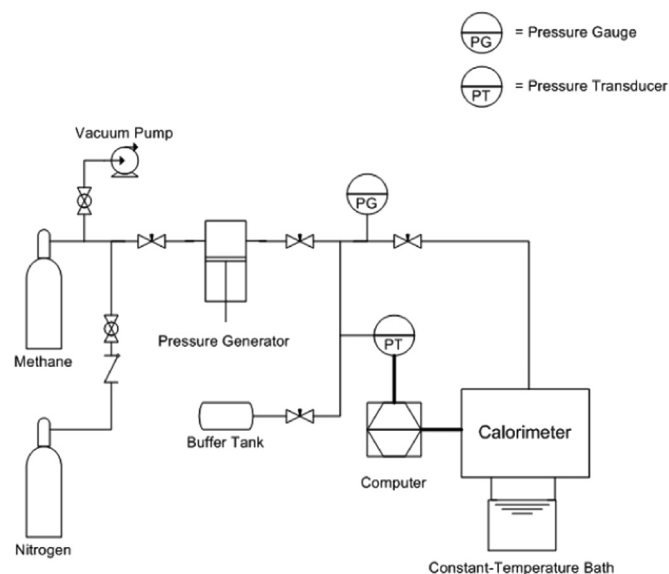


Fig. 1. High pressure DSC system.

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