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Hydrate risk management with aqueous ethylene glycol and electrolyte solutions in thermodynamically under-inhibition condition

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ABSTRACT

This study investigates the hydrate equilibrium conditions as well as the formation characteristics of monoethylene glycol and NaCl solutions by varying the concentration of NaCl from 3.5 to 20.0 wt% in an MEG solution. As predicted by the thermodynamic model, the hydrate equilibrium conditions were shifted toward lower-temperature and higher-pressure conditions. The equilibrium temperature depression data were interpolated linearly with the NaCl concentration in the MEG solution. The addition of NaCl affected the hydrate onset time and subcooling temperature only slightly, but their addition decreases the initial growth rate and hydrate volume fraction in the liquid phase. By increasing the NaCl concentration to 7.0 wt% in a MEG 20 wt% solution, the initial growth rate reduced to 0.2 vol%/min from 2.3 vol%/min of pure water, while the hydrate fraction was decreased to 18.7 vol% from 78.9 vol% of pure water; moreover, the torque change during the hydrate formation shows severe spikes for pure water with a maximum relative torque of 20 for the pure water. The addition of the 7.0 wt% NaCl to the MEG 20 wt% solution, however, only showed a negligible torque increase. The growth rate starts to decrease when the torque starts to rise for pure water, suggesting that the agglomeration of the hydrate particles may induce a mass-transfer limitation or slow down the particle growth. The presence of NaCl and MEG in the aqueous phase seems to minimize the interaction between the hydrate particles by surrounding the hydrate particle with the NaCl and MEG. These results proved that the NaCl plays a synergist role for the MEG in an under-inhibition condition by further limiting the hydrate fraction and minimizing the resistance-to-flow. This is the first work to present hydrate formation characteristics in the presence of both MEG and NaCl, and its insight will assist flow assurance engineers in the management of the risk of hydrate plug formation in offshore oil and gas fields.

1. Introduction

Gas hydrates are crystalline compounds that form when light hydrocarbon gases such as methane, ethane, and propane are incorporated into hydrogen-bonded water cages under high pressures and low temperatures (Sloan and Koh, 2007b). Subsea flowlines transporting hydrocarbon fluids in the multiphase are operated with an inherent risk of hydrate plug formation, where such pressure and temperature conditions can be readily achieved (Kim et al., 2014; Sloan and Koh, 2007b; Sloan et al., 2009). The typical industrial practice for the prevention of hydrate-related risks has been the injection of thermodynamic hydrate inhibitors including mono-ethylene glycol and methanol (Creek et al., 2011a, 2011b), and mono-ethylene glycol (MEG) is the preferred option for offshore gas fields to avoid health and safety issues for the operating platforms; however, the handling of large amounts of MEG or methanol in the offshore and remote areas where the platforms are located increases the operating cost significantly. It has been estimated that the cost of injecting thermodynamic inhibitors into subsea flowlines can reach 50% of the total operating costs for offshore fields producing about 50,000 bbl/day water (Sanford and Alapati, 2011).

When produced water contains various quantities of electrolytes, thermodynamic studies so far indicate they reduce the hydrate-formation tendency by shifting the hydrate equilibrium conditions to lower-temperature and higher-pressure regions (Ng et al., 1985; Song and Kobayashi., 1989). For deep-water gas-field development, the inhibition effect by the produced water is not sufficient to completely prevent hydrate formation, so MEG needs to be injected, resulting in aqueous solutions of MEG and electrolytes; moreover, for water-based drilling fluids, MEG and a variety of different electrolytes are mixed in their

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formulation (Li et al., 2005; Ning et al., 2010; Østergaard et al., 2000). Accurate knowledge of the hydrate-phase equilibrium is crucial to optimize the MEG concentration in aqueous solutions, and the effect of electrolytes on the equilibrium conditions must be addressed. In severe cases, the amount of MEG required to achieve a complete prevention of hydrate formation may render the offshore fields economically infeasible, requiring the consideration of an alternate approach for hydrate-risk management.

Attempts have been made to investigate the formation of gas hydrates when the MEG concentration is lower than the value required to fully prevent hydrate formation, known as *under-inhibition*. In principle, under-inhibition offers the prospect of support for a self-limiting fraction of hydrates in the flowline without the formation of the hydrate plug (Hemmingsen et al., 2008; Li et al., 2011). The aggregation and deposition of hydrate particles increase the resistance-to-flow in the flowline and may even lead to a hydrate plug formation. The highest resistance-to-flow was observed for systems with a water cut of approximately 60%, for which the oil-continuous condition existed for the majority of the hydrate-growth period whereby free water is available to bind both the hydrate aggregates and deposits (Sohn et al., 2015). In their work, the addition of 30 wt% of MEG in the aqueous phase reduced the hydrate fraction below 5 vol% and maintained the stable torque. Similar results were also observed when the gas-consumption profile and torque change were observed for the MEG 30 wt% solution during the hydrate-formation process, suggesting that the risk of hydrate plug formation can be managed using the under-inhibition strategy (Cha et al., 2013; Kim et al., 2014). When the MEG concentration is reduced below 20 wt%, the hydrates fraction in the aqueous phase increased up to 28 vol%, and their deposition may happen in the case of a low flow rate (Akhfash et al., 2013; Joshi et al., 2013); moreover, they focus on the hydrate-formation characteristics without a consideration of the presence of electrolytes, and more data will therefore be required to understand the hydrate-formation process for aqueous MEG and electrolyte solutions.

The salinity of produced water sometimes goes up to 300,000 mg/l (~30 wt%) (Ayers and Parker, 2001; Collins, 1975; Igunnu and Chen, 2012; Neff et al., 2011). Most research works for the gas hydrate in electrolyte solutions are limited to the reporting of the hydrate equilibrium conditions or the formation kinetics without a consideration of the MEG presence (De Roo et al., 1983; Dholabhai et al., 1997; Haghighi et al., 2009; Lee and Kang, 2011). Masoudi et al. (2005) developed a thermodynamic model based on a modified Patel–Teja equation of state with the NDD mixing rule whereby the binary interaction parameters between salts and ethylene glycols were determined. Their model predicted the hydrate equilibrium conditions of a methane-$CaCl_2$-MEG system, which showed a sound agreement between the model prediction and the experiment data. Increasing the MEG concentration from 14 wt% to 26 wt% depressed the hydrate equilibrium curve toward the lower-temperature region when the concentration of $CaCl_2$ was maintained at around 15 wt%, suggesting that MEG and $CaCl_2$ did not affect their inhibition performance. From the hydrate equilibrium studies for a synthetic gas mixture of methane, ethane, and propane in the presence of both ethylene glycol and electrolytes (NaCl, $CaCl_2$), the addition of NaCl on the same mass-percent basis showed more of a thermodynamic inhibiting effect than ethylene glycol (Sun et al., 2001). Chapoy et al. (2012) determined the water activity in ethylene-glycol and electrolyte (NaCl, $CaCl_2$, $MgCl_2$, KCl, NaBr) solutions, and then predicted the hydrate equilibrium conditions of methane and natural gas in the presence of ethylene glycol and NaCl. The experiment data were used to optimize the binary interaction parameters between the salts and MEG in terms of a modified Debye Huckel electrostatic. They combined the modified Debye Huckel electrostatic term with the Cubic-Plus-Association equation of state to take into account the effect of the ethylene glycol and electrolytes. An understanding of hydrate-formation kinetics is essential in the development of a hydrate management strategy as well as thermodynamics. The addition of small amounts of NaCl and clay lead to a decrease of the volume fraction of the hydrate in the aqueous phase, and the hydrate onset was delayed as well (Lee et al., 2002; Manteghian and Ahmadi, 2013). Long et al. (2015) observed that the initial growth rate decreased by adding NaCl and $MgCl_2$, while the kinetic-inhibiting effect of $MgCl_2$ is greater than that of NaCl. These studies suggested that the presence of electrolytes shifts the hydrate equilibrium conditions and reduces the hydrate growth rate; however, it is noted that the previous works were carried out mostly in the presence of electrolytes only, and the effect of the addition of MEG into electrolyte solutions on the formation characteristics of gas hydrates was not considered.

Despite considerable research on the hydrate equilibrium and formation kinetics in MEG and electrolyte solutions, limited data are available to describe the hydrate-formation characteristics when both MEG and electrolytes are dissolved in the aqueous phase. In this work, a new experimental measurement of the hydrate equilibrium conditions in the presence of both MEG and NaCl in the aqueous phase, while the concentration of NaCl is varied from 3.5 to 20 wt% is conducted; moreover, the hydrate-formation characteristics of the MEG and NaCl solutions were studied by measuring the hydrate-onset time, growth rate, hydrate fraction, and torque changes. The obtained results were employed to develop the hydrate management strategy for the subsea flowlines that transport natural gas with electrolyte-containing produced water.

2. Materials and methods

2.1. Experiments

A synthetic natural gas, which was composed of 90.0 mol% CH_4, 6.0 mol% C_2H_6, 3.0 mol% C_3H_8, and 1.0 mol% n-C_4H_{10}, was supplied by Special Gas (Korea). Mono-ethylene glycol (99.5% purity) was purchased from JUNSEI. The sodium chloride (NaCl) (99.5% purity) was used in this study as a representative electrolyte in the produced water and was also provided by JUNSEI. Deionized water (99.0% purity) was used without further purification. The maximum salinity of the produced water was set to 20 wt% of NaCl in consideration of the maximum soluble mass of NaCl at 273.15 K, which is 25.62 g per 100 g of the aqueous MEG solution (Masoudi et al., 2004).

A high pressure autoclave was used to investigate the hydrate equilibrium conditions and the formation kinetics, whereby the pressure, the temperatures of the fluids, and the torque changes of the mechanical stirrer were monitored during the hydrate-formation and hydrate-dissociation processes. The autoclave is made of 316 SUS with an anchor-type impeller that is used to mix the fluids. The impeller was located on the base of the shaft and the torque of the rotating shaft was measured using a torque sensor (TRD-10KC) that comprises a platinum-coated connector with an uncertainty of 0.3%. Huo et al. (2001) suggested the motor current as an indicator of a hydrate plug formation in high pressure apparatuses. Once a plug is formed, the impeller needs to overcome the friction between the hydrate plug and the hydrocarbon fluid, resulting in a higher torque or motor current. Akhfash et al. (2016) and Aman et al. (2014) used the change of the motor current to investigate the changes of the rheological properties of the aqueous MEG solution as well. The pressure was measured by transducers with an uncertainty of 0.01 MPa. The cell was immersed in a water bath that can control and maintain the temperature of the autoclave. The temperatures of the gas and the liquid phase were measured using a platinum-resistance thermometer with an uncertainty of 0.15 K. The torque, pressure, and temperature data were recorded through a data-acquisition system in real time.

A preliminary investigation was carried out by measuring the hydrate-dissociation conditions using an isochoric step-heating method at NaCl concentrations of 3.5 wt%, 7 wt%, 10 wt%, and 20 wt%,