



Phase equilibrium data of methane hydrates in mixed brine solutions

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ABSTRACT

Knowing the hydrate phase equilibria in brines is critically important to assess the risk of hydrate formation, especially for conditions involving high salinity and very high pressure, which are becoming more prevalent in oil/gas exploration and production. Hydrate phase equilibria data for mixed salt brines over a wide range of pressure is very limited in the open literature. Inorganic salts are thermodynamic hydrate inhibitors and are commonly present in produced water from oil/gas production. As such, this study reports methane hydrate phase equilibria in brines composed of mixed salts (NaCl, KCl, CaCl₂ and MgCl₂) for total salt concentration up to 29.2 wt% and for pressures ranging from 20 to 200 MPa (2900 to 29,000 psia). Data under these conditions are the first reported and they add significant value in furthering knowledge of the phase space for hydrate formation. In addition, these data are used for the development and assessment of models to capture hydrate phase equilibria over a wide range of salt concentrations and pressures. At last, critical factors (such as pressure, salt species, and concentration) that influence the hydrate suppression temperature relative to the uninhibited (salt-free) systems are also investigated.

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1. Introduction

Gas hydrates are stabilized by entrapping either light hydrocarbon (e.g., methane, ethane, propane) or non-hydrocarbon (e.g., carbon dioxide, hydrogen sulfide, nitrogen) gases inside cavities formed from the hydrogen-bonding of water molecules (Sloan and Koh, 2007). The crystal structure of the hydrate formed is mainly determined by size of the guest molecules and their interactions with the water molecules (Holder et al., 1988).

Gas hydrates are of great interest for both scientific and practical reasons. Hydrates store a large amount of gas in a condensed solid phase, making them suitable for energy storage and transportation, as well as carbon sequestration (Goel, 2006; Gudmundsson et al., 1994; Park et al., 2006; Sun et al., 2003). In addition, since hydrates can only form from free water not associated with the

solvation of dissolved salts, the hydrate formation can be utilized as a separation process for both water (e.g., seawater desalination (Barduhn, 1967)) and gas. Inversely, hydrates can be hazards to seafloor stability and may play a role in climate change (Pecher et al., 2005). Naturally occurring hydrate deposits in the deep ocean sediments can dissociate/destabilize, potentially causing underwater subsidence or landslides, and as such, resulting in methane to be released to the environment (ocean water and atmosphere), where it can be oxidized to carbon dioxide, exacerbating climate change (Ruppel and Kessler, 2016). Moreover, hydrates are considered a nuisance in the oil and gas production and operations, since the low seabed temperature and the presence of water and gas are prone to hydrate formation, leading to solid accumulation in flowlines that could potentially restrict flow and eventually form blockages.

It is well known that inorganic salts are thermodynamic hydrate inhibitors, shifting the hydrate dissociation conditions to lower temperature and higher pressure (Hu et al., 2017a,b,c), since in aqueous solution, the dissolved ions tightly bound water molecules through electrostatic forces. Salts commonly exist in produced water and are also widely prevalent in the oil/gas production. The major electrolytes present in seawater and produced water are Na⁺, K⁺, Ca²⁺, Mg²⁺, Ba²⁺, Br⁻, Cl⁻, CO₃²⁻, and SO₄²⁻ (Blandamer et al., 2005; Tanveer and Chen, 2016). The development and production

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of oil/gas in pre-salt layer reservoir in Gulf of Mexico, a layer of oil bearing rock of carbonate composition, are positioned at depths between 5000 m and 6000 m below sea level, in ultra-deep water (1900 m to 2400 m) beneath a thick salt layer (in some areas up to 2000 m), resulting in reservoir pressures higher than 100 MPa (14,500 psia) and salt concentrations more than 20 wt% (Estrella, 2011). Besides, brines are usually added to water-based drilling fluids for offshore exploration to avoid clay swelling (Halliday et al., 1998), while heavy brines are used during well completion to offset the high reservoir pressures with the high brine hydrostatic pressure and prevent a well blowout (Erdogmus et al., 2005). If a well is drilled in the offshore environment, both the high hydrostatic pressure of the column of fluids and low seabed temperature are conducive for hydrate formation in the drilling string, blow-out preventer and choke line in the event of gas kick with light hydrocarbon gases migrating into the wellbore and contacting with the cold brine. Hydrate formation in brines could lead to continuous increase of salinity and fluid density, and consequently cause salt precipitation. Moreover, the accumulation of solids (salts and hydrates) could finally result in a solid blockage, eventually restricting flow and posing severe risk of pressure build up during oil and gas exploration, production and transportation. Therefore, it is of great fundamental and practical importance to investigate the hydrate dissociation conditions in brines, which are often composed of mixed salts, to understand and develop uses of hydrates, including hydrate prevention, management and remediation, seawater desalination, and methane hydrate exploration.

In the past decade, a number of studies focused on the measurements of hydrate formation in mixed electrolyte aqueous solutions (Atik et al., 2009; Dholabhai et al., 1991; Dickens and Quinby-Hunt, 1994; Englezos and Bishnoi, 1991; Englezos and Ngan, 1993; Maekawa and Imai, 1996; Tohidi et al., 1997). However, most of the data in the open literature are for systems with low salt concentration (close to seawater salinity, i.e., 3.5 wt%), and moreover, all are measured for pressures below 34.5 MPa (5000 psia), which does not cover the wide range of conditions to be encountered for more recent deep water oil/gas field development and production. As oil and gas fields delve into deeper water depths, the harsh conditions in terms of high pressure and salinity requires reliable hydrate phase equilibria in brine systems over a wide range of conditions in terms of both salt concentration (up to saturation) and pressure (up to 200 MPa/29,000 psia) (Arrieta et al., 2011; Estrella, 2011). Current prediction tools commonly used for hydrates are not tested and benchmarked for conditions in terms of pressure and salinity considered in deep water developments since no experimental data are available, leading to large uncertainty of predictions, which consequently imposes severe flow assurance challenges, such as loss of production, pressure build up and flowline damage. Therefore, in this study, the measurements of methane hydrate phase equilibria in mixed salts brines, including NaCl, KCl, CaCl₂ and MgCl₂, are performed with total salt concentration up to 29.2 wt% and for pressures ranging from 20 to 200 MPa (2900 to 29,000 psia). The phase equilibrium data obtained in this study are applied to not only investigate the effect of pressure and salt on the hydrate suppression, but also evaluate the performance of commonly used prediction tools and developing correlations for estimating hydrate suppression temperatures in inhibited systems.

2. Experimental method

Table 1 summarizes the purities and suppliers of salts and gases used in this work. A summary of the salt compositions and total salt concentration of aqueous solutions tested in this study are listed in Table 2. For each experiment, approximately 50 g of aqueous salt

solution is prepared by adding nanopure water to solid salt crystals according to the compositions in Table 2. All solutions are prepared gravimetrically and the composition uncertainty is ± 0.004 wt%.

For each experiment, a 56 mL pressure cell is filled with 25 mL of aqueous solution, which is continuously stirred with a magnetic bar coupled with a strong external magnetic mixer at 500 rpm. The baffle in the cell allows for good mixing in the cell between the gas and liquid phases. The cell is immersed into a thermostated bath where the temperature can be controlled from 238.15 to 333.15 K, maintained by a refrigeration/heating circulator connected with a coolant bath containing a propylene glycol-water mixture. After flushing the system three times with methane gas to remove air and impurities, the system is pressurized to the desired pressure with a gas booster pump. During the experiment, the pressure cell is isolated from the manifold by a valve installed on the gas injection line downstream of the hand pump. The system conditions are monitored by a resistance temperature detector (RTD) and a pressure transducer, which have uncertainty of ± 0.25 K and 0.05% full scale output, respectively. Three phase (liquid-hydrate-vapor) equilibrium points of methane hydrate in mixed electrolyte aqueous solutions are measured via an isochoric method including the following procedure shown in Fig. 1: (i) fast cooling (linear decrease of pressure-temperature data with no hydrate), (ii) hydrate formation (sudden pressure drop and exothermic process), (iii) fast heating at a rate of 5 K/hr, and (iv) slow stepwise heating. The stepwise heating is used since the system is continuously changing and equilibrating during hydrate dissociation, in terms of the amount of the phases present and the salt concentration in solution (Lafond et al., 2012). During the process of stepwise heating, the temperature is increased by 0.2 K and maintained for 1.5 h until the system pressure stabilizes. Finally, the three-phase equilibrium point is determined by the inflection point, where the hydrate dissociation and the heating/cooling lines intersect. This methodology for hydrate phase equilibrium measurements has been extensively used as a reliable and robust experimental method. In our previous studies, we have shown the consistency, repeatability and reproducibility of data measured with the experimental system using this described methodology. Further detailed description of experimental apparatus and procedure are reported elsewhere (Hu et al., 2017a,b,c).

3. Results and discussion

The measured data of methane hydrate phase equilibria in the presence of mixed salts (NaCl, KCl, CaCl₂ and MgCl₂) with the specific composition shown in Table 2 at pressures ranging from 20 to 200 MPa are plotted in Fig. 2 and summarized in Table 3. Since no open literature data of methane hydrate phase equilibria in mixed salt brines are available at the pressure range considered, the experimental data measured in this study are very valuable, in particular to develop and validate predictive models. In the absence of other data, we compare the measured data with the predictions for methane hydrate phase equilibria from two tools: i) the first tool, to be denoted as P₁ (PVTsim, 2016), is based on the van der Waals and Platteeuw model (Van der Waals and Platteeuw, 1959)

Table 1
Information of materials used in this study.

Chemical	Supplier	Purity
Methane (CH ₄)	General Air	99.97% mol
Sodium Chloride (NaCl)	Macron Fine Chemicals	>99% mol
Potassium Chloride (KCl)	Fluka Analytical	>99.9995% mol
Calcium Chloride (CaCl ₂)	Macron Fine Chemicals	>99% mol
Magnesium Chloride (MgCl ₂)	Sigma-Aldrich	>98% mol

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