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Gas hydrate formation from high concentration KCl brines at ultra-high pressures

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ABSTRACT

The phase equilibria of methane hydrates were measured in high concentration KCl brines (up to saturation concentration) at ultra-high pressures (up to 200 MPa). The results show the hydrate equilibrium boundary moves to lower temperature and higher pressure as the KCl concentration increased up to the saturation limit and the hydrate equilibrium is unchanged from the saturation concentration for four-phase equilibrium. From the measurements at the saturation concentration, we also determine the pressure effect on the solubility of KCl. The kinetic studies reveal hydrates form even with salt precipitated and hydrates and salt are competing solid precipitation under saturated conditions.

Introduction

Gas hydrates are icy inclusion compounds formed by small guest molecules, such as methane (CH_4), ethane (C_2H_6), propane (C_3H_8), carbon dioxide (CO_2) and hydrogen sulfide (H_2S), occupying the cavities formed by hydrogen-bonded water molecules. The hydrate crystal structure formed depends on the shape and size of guest molecules and formation conditions. The most commonly encountered structures are the cubic structures I (sI) and II (sII) [1].

In the last two decades, much of the hydrate literature has focused on the chemical and physical properties of hydrates, especially applied to the areas of hydrates as a future energy resource [2–7] and as a problem in the production and transportation of oil and gas [1,8,9]. For the petroleum industry, exploration, development and production of oil fields in ultra-deep water depths (>1500 m) are becoming more common [10]. Many of the oil reservoirs at these depths are pre-salt fields, which are positioned below sea level (depths, ~6000 m) in ultra-deep water beneath a thick salt layer, resulting in reservoir conditions exceeding 100 MPa in pressure and produced water at salt saturation [10,11]. These harsh conditions cause significant challenges in the production, in particular with respect to hydrate formation, as the high pressure also translates in higher formation temperature while higher salt concentration depresses the formation temperature [10–16].

Only recently our group reported the first open study [11] on the gas hydrate phase behavior and kinetics from high concentration NaCl brines (up to saturation concentration) at ultra-high pressures (up to ~200 MPa). The formation of gas hydrates under these extreme conditions revealed: (i) the hydrate phase equilibrium boundary moves to lower temperature and higher pressure as the salt concentration increased up to the saturation limit; (ii) the hydrate equilibrium is unchanged from the conditions at saturation with four-phases (CH_4 [g] – NaCl solution [l] – Hydrate [s] – NaCl precipitated [s]) in equilibrium; (iii) hydrates can still form even with salt precipitated; and (iv) the formation of hydrates and salt precipitation are competing effects at saturated conditions.

To further our understanding of hydrates under harsh pressure and concentration conditions, we report here experimental measurements of hydrate phase equilibria and kinetics for various concentrations of KCl (potassium chloride) brines (0, 20, 23, 25.4, 30 and 40 wt% KCl), which is one of the major chloride salts

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dissolved in the produced water from pre-salt oil fields (the reported study here is part of a larger study we have done on chloride salts, and the data for the other salts are forthcoming in other publications). Measurements of hydrate phase equilibria were made for three-phase (KCl solution [l] – Hydrate [s] – CH_4 [g]) or four-phase (KCl solution [l] – Hydrate [s] – KCl precipitated [s] – CH_4 [g]) equilibrium depending on the salt concentration. From the measurement with 25.4 wt% KCl, the phase transition from precipitated salt (four-phase) to dissolved salt (three-phase) was found at around 287 K and 56.4 MPa. Using these conditions, we were able to investigate the pressure effect on the KCl solubility in water [17,18]. Our measurements in the kinetic experiments also showed the competing precipitation of KCl and hydrates, similarly to that reported for NaCl [11], demonstrating and supporting the interplay of hydrate formation and salt precipitation. The reported data represent fundamental knowledge to understand the physical chemistry of hydrates in brines and essential in the application of gas hydrates in the flow assurance of oil and gas production and seawater desalination.

Experimental section

A recently developed system [11,19] for ultra-high pressure experiments is used to measure the hydrate phase equilibrium and formation kinetics in high salinity systems with KCl. The experimental system has been described in detailed elsewhere [11]. We briefly describe it here in the context of this study. This system has an operating pressure limit of 207 MPa and can be temperature controlled from 238.15 to 333.15 K. To protect the experimental system from corrosion due to salt, all parts (pressure cell lining, baffle, resistance temperature detector) in direct contact with brine solution were made of Inconel 600. For all experiments, 25 ml of brine solution was inserted into the cell. The solutions considered contained 0, 20, 23, 25.4, 30 and 40 wt% KCl (potassium chloride, >99.9995% purity, Fluka Analytical). Note that the saturation concentration of KCl at 293.15 K is approximately 25.4 wt% [20]. For the 30 and 40 wt% KCl, the solution was at saturation and the excess salt present as solid precipitate. Once sealed, the pressure cell was immersed into the coolant bath containing a propylene glycol-water mixture, which is connected with a refrigerated/heating circulator. A baffle, magnetic bar and magnet plate stirred at 500 rpm allows for effective mixing between the gas and liquid. Before starting any experiment, the system was flushed three times with the experimental methane gas (>99.97%, General Air) to remove air and other impurities, and then the cell was pressurized to the desired pressure using a gas booster.

For the measurements of the hydrate phase equilibrium, an isochoric method [1,11] was used with the following procedure: (i) fast cooling, (ii) hydrate formation (identified by sudden pressure drop and temperature raise), (iii) fast heating at a rate of 5 K/h, and (iv) slow stepwise heating to dissociate hydrates and return the system to its initial state. This procedure is shown in Fig. 1(a). We should note that hydrates sometimes formed during the fast cooling period or even during the fast heating period, as the conditions are still under the hydrate stable region, but in all cases, the pressure-temperature data returned to the gas expansion/contraction line after hydrates completely dissociated. The intersection represents the phase equilibrium point. For step (iv), the temperature is stepwise increased (~90 min for each step), as shown in Fig. 1(b), so that the system pressure stabilizes at each temperature, allowing the phases to equilibrate for gradual hydrate dissociation and solution salinity.

For the kinetic experiments, a high concentration (30 wt%) KCl brine – concentration above KCl saturation at ambient conditions [20] – was placed in the pressure cell and the system was pressurized up to 128 MPa with methane gas at 313.15 K, corresponding to condition outside the hydrate stable region. After reaching steady conditions, the cell was cooled to 278.75 K in a fixed volume system, and temperature and pressure in the cell was respectively monitored over time to measure the rate of hydrate formation.

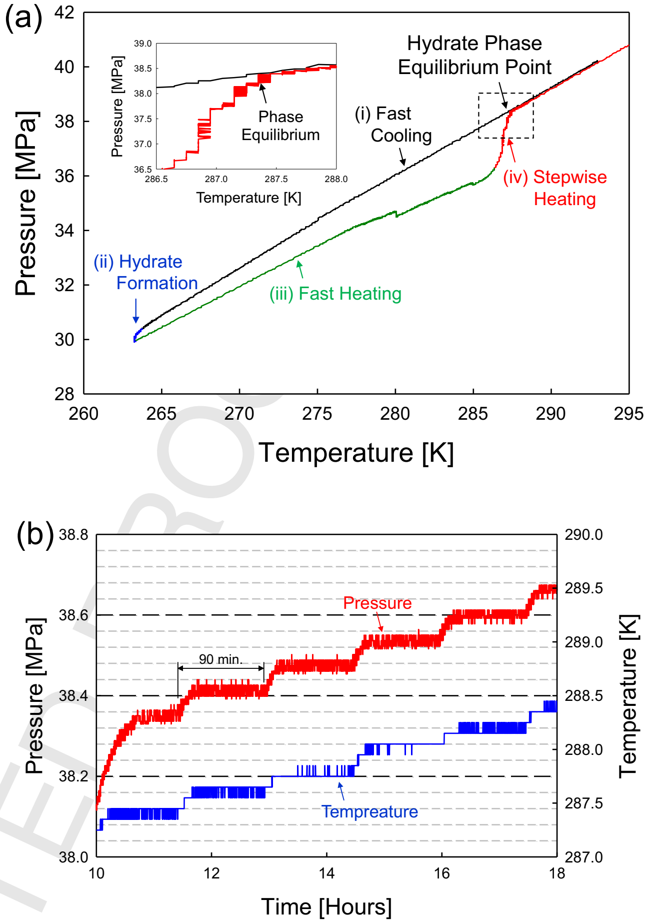

Fig. 1. Description of experimental procedure for the measurements of hydrate phase equilibrium via the isochoric method. (a) Example of pressure and temperature trace for hydrate formation and dissociation in the 20 wt% KCl system. Inset shows the slope change of the heating curve as the hydrate phase equilibrium point is reached. (b) Pressure (red) and temperature (blue) traces showing the stepwise increase in temperature, maintained for about 90 minutes until the pressure stabilizes. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Results and discussion

Methane hydrates phase equilibria with KCl brines

Our recent study [11] introduced the phase behavior for gas hydrates formed from high concentration NaCl brines at ultra-high pressures. In that study, the hydrate phase equilibrium boundary was measured and shown to shift to lower temperature and higher pressure as the NaCl concentration increases up to the limit of salt saturation in solution; the hydrate equilibrium is unchanged with excess NaCl beyond the saturation concentration, corresponding to conditions at the quadruple point. Here, in this study with KCl, we observe similar phase behavior for methane hydrates up to 200 MPa. Fig. 2 shows the measured data, all above 18 MPa, and the existing literature data, all below 18 MPa (see the Supplementary information for the actual values of the measured data). The measured data clearly fills a large phase space, in terms of

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