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EXPERIMENTAL PHASE EQUILIBRIUM FOR METHANE HYDRATES IN INHIBITED SYSTEMS

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Abstract. *High pressure and low temperature conditions inside subsea oil and gas flowlines, coupled with the presence of water and light hydrocarbons provide the necessary thermodynamic conditions for gas hydrate formation, which can eventually lead to flowline blockage. In this work, experimental dissociation data for inhibited methane hydrates are reported at different temperatures with sodium chloride and monoethylene glycol. The experiments were conducted through isochoric method. The experimental methodology reliability is assessed comparing the obtained experimental data with the data reported in the literature for pure methane hydrates.*

Keywords: *gas hydrate, methane, thermodynamic inhibitor, phase equilibrium*

1. INTRODUCTION

Hydrate issue is one of the major problem in the oil and gas industry due to hydrocarbon pipeline blockage. Clathrate hydrates are crystalline, non-stoichiometric solids consisting of guest gas molecules surrounded by hydrogen-bonded cages of water molecules (Sloan and Koh, 2008). Three types of clathrate hydrate structures are known which are classified based on the size of the guest molecules and their interaction with the water molecules: structure I, II and H. High pressure and low temperature conditions inside subsea oil and gas flowlines, coupled with the presence of water and light hydrocarbons provide the necessary thermodynamic conditions for gas hydrate formation, which can eventually lead to flowline blockage. The safety and economic risks associated with hydrate in flow assurance have been one of the most important motivations for studies. To prevent hydrate plugging, thermodynamic hydrate inhibitors (methanol, ethylene glycol, salt-electrolytes) are used. These substances shift hydrate equilibria conditions to higher pressure and lower temperature (Sloan and Koh, 2008). Thus, reliable experimental data for gas hydrate phase equilibrium in the presence of inhibitors are therefore necessary to avoid hydrate plug formation in subsea oil and gas flowlines.

In this work, experimental dissociation data for methane hydrates in the presence of sodium chloride and monoethylene glycol aqueous solutions were carried out based on isochoric method. Additionally, the experimental data for the studied systems were compared with some selected experimental data from the literature to demonstrate the reliability of the experimental methodology.

2. EXPERIMENTAL

2.1 Apparatus

High-pressure autoclave apparatus was used for the study of hydrate formation and dissociation as shown in a schematic diagram Fig. 1(a) and the picture in Fig. 1(b). The autoclave was designed to measure phase equilibrium conditions of gas hydrates. The apparatus consists of autoclave (a high pressure cell) (1), which has a maximum volume of 500 cm^3 and can operate at pressure up to 25 MPa, a circulating bath Polyscience PP15R-40 (2) and a data acquisition system (10). The temperature control of the autoclave is responsible for circulating a mixture of water and monoethylene glycol from the thermostatic bath (2) to the container-circulating bath (3). Also a temperature sensor (PT100) (7) is used to measure the temperature inside the autoclave in the 263-423 K range with an accuracy of 0.1 K and a pressure transducer (6) is used to monitor the pressure of the autoclave (measurement uncertainty of 0.03MPa).

The aqueous solution inside the autoclave is mixed with a four-blade stirrer (8) connected with an electric motor (9) through a magnetic coupling. A booster pump (4) injects the gas into the autoclave at the specified pressure. The system control and recordings of pressure and temperature data are performed using a National Instruments hardware and Labview software package (10).

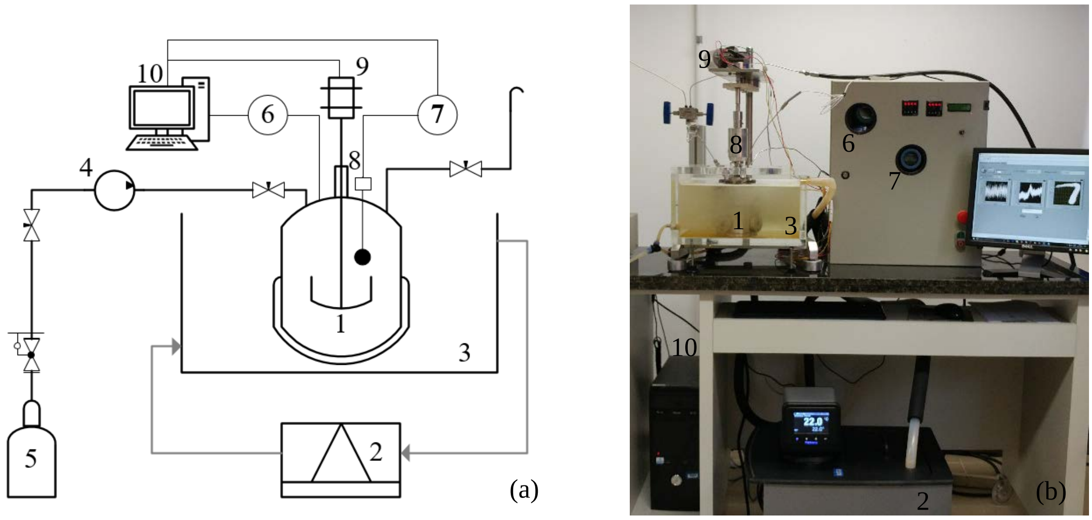

Figure 1 (a). Schematic diagram and (b) image of the Experimental Setup. 1 – Autoclave; 2 –Thermostatic bath; 3 – Container circulating bath; 4 – Gas booster; 5 – Gas cylinder; 6 – Pressure sensor; 7 – Temperature sensor; 8 – Blade stirrer; 9 – Electric motor; 10 – Acquisition system.

2.2 Materials

In all experiments methane gas having a purity of 99.999% was used and was supplied by the White Martins. Vetec and Biotec provided sodium chloride P.A. (NaCl) and monoethylene glycol P.A. (MEG), used for preparing different samples in distilled water, respectively. Table 1 summarizes the experiments carried out in terms of inhibitor, concentration in the aqueous solution and initial pressure.

Table 1. Composition and experimental pressures of different phase equilibrium samples

Sample number	Inhibitor	Composition (wt%)	Initial pressure (MPa)				
S1	NaCl	5	6.5	7.0	7.5	8.0	
S2	NaCl	15	7.0	8.0	9.0	10.0	
S3	MEG	5	5.5	6.5	7.5	8.5	9.5
S4	MEG	10	6.5	7.5	8.5		
S5	MEG	20	5.5	12	15	20	

2.3 Procedure

The isochoric method to measure hydrate phase equilibria conditions was used. Samples of aqueous solutions containing the inhibitor was prepared gravimetrically. Certain volume of samples (100 ml) was placed into the autoclave. The free volume of the autoclave was filled with gaseous methane in the initial pressure informed in Table 1 at room temperature through booster pump. After gas injection, the blade stirrer was turned on at the rate of 60 rpm and the system was cooled 10 degrees below the hydrate equilibrium temperature, which correspond to the three-phase equilibrium conditions (L_w-H-V) for the system at a given pressure. At this value of temperature, the autoclave was thermostated for 24 h. The onset of hydrate phase in the system was observed by rapid pressure drop. After the hydrate formation, the system was heated to 1 K below of the estimated equilibrium temperature of hydrate decomposition (this temperature value was estimated using the software CSMGem (Ballard, 2002)). The temperature in the autoclave was subsequently increased at a slow heating rate of 0.05 K/h. Complete dissociation of the gas hydrates was detected by crossing the cooling and dissociation curves. Following, the cell was heated to the initial temperature to guarantee that no gas leakage had occurred.

3. RESULTS

In this study, experimental data have been done on the methane hydrate formation and dissociation in presence of sodium chloride or monoethylene glycol, varying concentrations in 0.05, 0.10, 0.15 mass fraction and 0.05, 0.10 and 0.2 mass fraction, respectively.

The initial conditions of temperature and pressure were set at 295.15 K and pressures listed in Table 1 for each experiments. Temperature and pressure diagram for 0.20 mass fraction of monoethylene glycol is shown in Fig. 2. At initial conditions, a linear pressure drop was observed due to dissolution of gas in water in region AB known as 'sub cooling' region. After some hours of sub cooling region, a sharp drop in pressure occurred indicating the nucleation of hydrate crystals (point B) at which the hydrate formation initiated. This observed pressure drop is due to conversion of large number of methane molecules into hydrate and simultaneous decrease in temperature. After nucleation, pressure continues to decrease rapidly due to the growth of hydrate crystals. After a certain point, there is no drop in pressure observed. At point C, dissociation was conducted by fast heating and after, slow and step-wise heating from the point D to bring the system out of the hydrate formation region. As temperature increases, the pressure of the system also increases due to thermal expansion of the methane gas and disturbance of the hydrate equilibrium system. Point A (Thermodynamic equilibrium point) again denotes the completion of dissociation where heating curve meets the cooling curve as shown in Fig. 2.

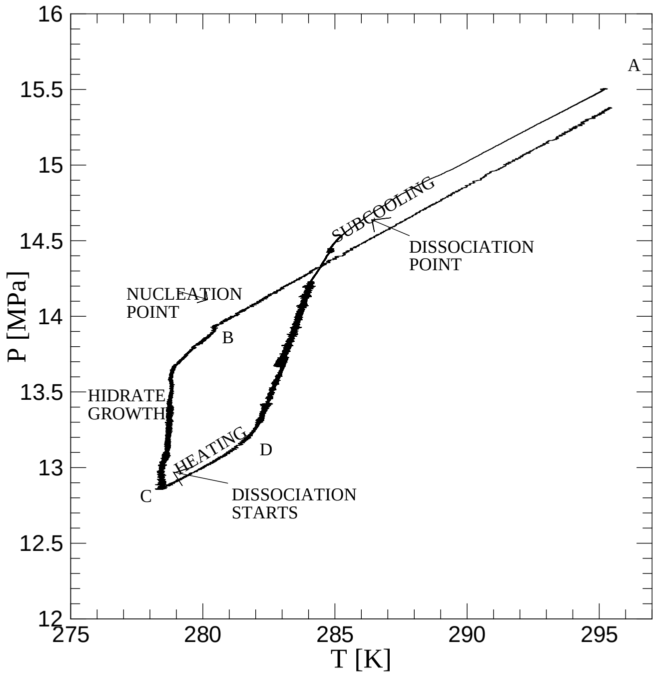

Figure 2. Experimental Procedure for hydrate equilibrium point [curve of 0.02 monoethylene glycol + H_2O + CH_4]

The accuracy of experimental procedure was verified with experimental data for phase equilibrium conditions in the system of CH_4 + H_2O reported in a previous study (Kakitani *et al*, 2017).

During formation of hydrates, the three phase equilibrium is not established as hydrates are formed at super-cooling state. However, during the dissociation stage, the three phase equilibrium is established and considered as the true phase equilibrium of the system. All dissociation data measured in the present work were reported in Table 2 and were plotted in Fig. 3 to show thermodynamic inhibition effects on the hydrate formation. In all systems, the compositions of the gas and liquid phases are constant during the hydrate formation and dissociation processes.

Table 2. Experimental dissociation data for methane hydrates in the presence of NaCl and MEG aqueous solutions.

0.05 mass fraction NaCl		0.15 mass fraction NaCl	
T [K]	*P* [MPa]	*T* [K]	*P* [MPa]
279.94	5.956	274.65	6.386
280.11	6.250	275.99	7.244

280.69	6.673	276.88	8.199
281.01	7.053	277.54	9.192

0.05 mass fraction MEG		0.10 mass fraction MEG		0.20 mass fraction MEG	
T [K]	*P* [MPa]	*T* [K]	*P* [MPa]	*T* [K]	*P* [MPa]
278.98	5.221	280.11	6.249	275.051	4.659
280.68	6.145	280.96	6.996	283.641	10.943
282.08	7.139	282.51	8.318	284.723	14.349
282.83	7.861			287.412	20.573
284.09	8.944				

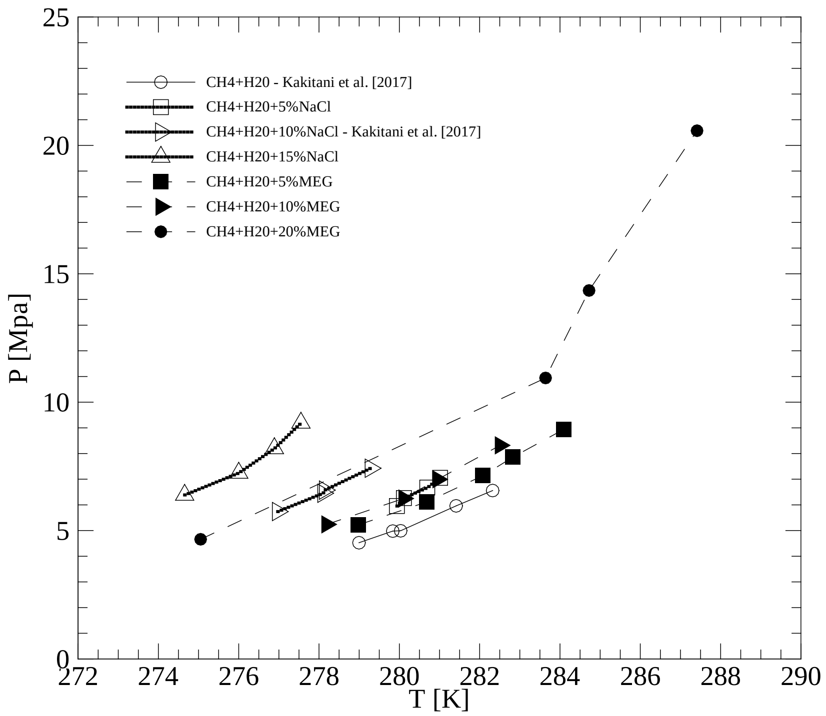

Figure 3. Experimental dissociation conditions of methane hydrates in the presence of inhibitors aqueous solutions. Symbols represent experimental dissociation conditions: □ 0.05 NaCl this work; △ 0.15 NaCl this work; ■ 0.05 MEG this work; ► 0.10 MEG this work; ● 0.20 MEG this work; ○ pure water and 0.10 NaCl literature data.

It was observed that the inhibition effect means shifting hydrate dissociation conditions to high pressures/low temperatures due to the presence of salt/glycol in aqueous solution. The hydrate dissociation temperature decreases with increasing NaCl concentration. Sodium chloride ionizes in solution and has strong electrostatic interactions with the water molecules. The water solvating the dissolved ions are unable to form hydrates and as such, a lower temperature is needed to order the water molecules with the CH_4 molecules for hydrates to form (Sloan and Koh, 2008). As a secondary effect, the addition of NaCl in water brings about the salting-out effect, which reduces the activity of water. The action of glycol as hydrate inhibitor is different from that of the sodium chloride. The hydrogen bonding of the hydroxyl group in glycols with water molecules is the only molecular interaction that ties up water molecules making them unavailable to form hydrates.

Moreover, it was included an analysis of literature experimental data [Roo *et al.*, 1983, Haghighi *et al.*, 2009, Cha *et al.*, 2016, Kakitani *et al.*, 2017] for NaCl and [Robinson *et al.*, 1986, Haghighi *et al.*, 2009, Mohammadi *et al.*, 2010] for MEG, related to the dissociation conditions of methane hydrates in the presence of inhibitors, which were presented in Fig. 4 and Fig. 5.

The acceptable agreements between the experimental data measured in this work and the experimental data reported in literature demonstrated the reliability of the experimental technique and the accuracy of the new data reported in this work. The deviations between the experimental data are within ±0.8 K.

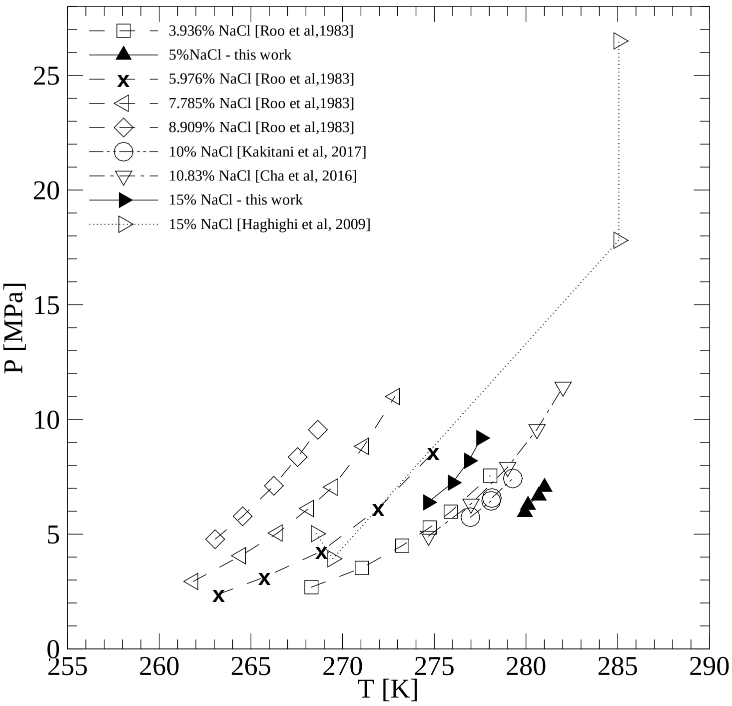

Figure 4. Literature data for CH_4 hydrate in NaCl systems compared to this work.

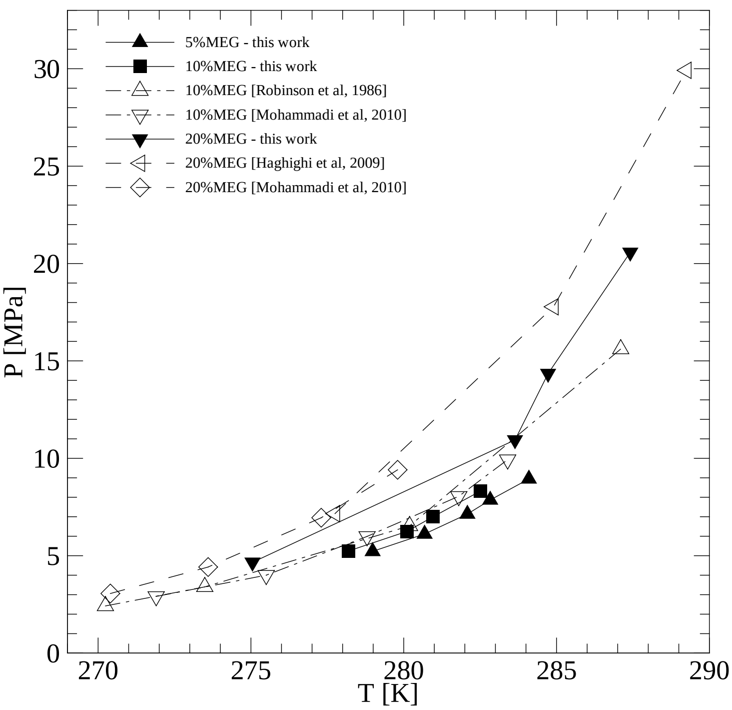

Figure 5. Literature data for CH_4 hydrate in MEG systems compared to this work.

4. CONCLUSIONS

New equilibrium data for methane hydrates inhibited with sodium chloride and monoethylene glycol were experimentally reported at temperatures ranging from 274.65 to 287.41 K and pressures up to 20 MPa using the isochoric method. The experimental three-phase equilibrium data (L_W-H-V) were compared with those in the literature, showing consistent agreement.

5. ACKNOWLEDGEMENTS

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