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Incipient Equilibrium Gas Hydrate Formation Conditions for The $\text{CO}_2\text{-CH}_4\text{-Neoohexane-NaCl-H}_2\text{O}$ and $\text{CH}_4\text{-Polypropylene Glycol-NaCl-H}_2\text{O}$ Systems

by

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Abstract

Incipient equilibrium hydrate formation pressures for the methane-carbon dioxide-neohexane-sodium chloride-water system were measured between 274.1 and 276.2 K. In addition, similar data were obtained for the methane-polypropylene glycol-sodium chloride-water system at temperatures ranging from 274.2 to 282.7 K. The isothermal pressure search method was employed to locate the minimum pressure at a constant temperature. The concentration of methane on a water-free basis was 50 % in the methane-carbon dioxide gas mixture.

Key Words : Hydrate Equilibrium Data, Methane, Carbon Dioxide, Neohexane, Sodium Chloride

I. Introduction

Clathrate or gas hydrates are non-stoichiometric crystals formed by the enclosure of molecules like methane, carbon dioxide and hydrogen sulfide inside cages formed by hydrogen-bonded water molecules. There are more than 100 compounds (guests) that can combine with water (host) and form hydrates. Among these chemicals are natural gas components¹⁾. Consequently, a large number of equilibrium hydrate formation data have been collected over the years in order to facilitate the safe design of processes in relevant oil and gas operations^{2,3)}. For example, drilling equipment can be severely damaged during drilling through hydrate layers. In addition, hydrate formation in water based drilling fluids can cause subsea equipment to become plugged and cause difficulty with subsequent operations⁴⁾.

Gas hydrates are a special type of inclusion compounds. There is no chemical bonding between the host and guest molecules. The hydrate crystals may exist at temperature below and above the normal freezing point of water. Two hydrate crystal structures (structure I and II) were recognized since the late 1940 s. Hydrate forming molecules like methane and carbon dioxide are trapped in the

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cages of these structures. In 1987, the National Research Council (NRC) of Canada^{5,6)} reported a new structure (structure H). The unit cell has two small cages like the other two structures and one large cage. The large cage is occupied by larger molecules like neohexane that stabilizes the structure while the small cages are filled with methane or nitrogen or argon.

The above mentioned three gases are the only known light components that participate in structure H hydrate formation. Experiments at NRC showed that carbon dioxide with neohexane and ice formed structure H hydrate⁷⁾. There could be serious implications for the use of carbon dioxide in secondary oil recovery if structure H hydrate forms in these systems because the design of the facilities would then have to be such that hydrate formation is prevented. Experiments were carried out in our laboratory with carbon dioxide and liquid water but it was not possible to obtain hydrates of structure H. The hydrate that was formed was stable within the carbon dioxide structure I hydrate equilibrium conditions⁸⁾. Hence, experiments were done with a 80-20 and a 50-50 mole % methane-carbon dioxide gas mixture⁸⁾. The results showed that the 80-20 % methane-carbon dioxide gas mixture together with -2,2-dimethyl butane (neohexane) form structure H hydrate whereas the 50-50 % gas mixture may only form that structure below 277.5 K⁸⁾.

In the present work, the 50-50 % methane-carbon dioxide gas mixture is used to obtain equilibrium hydrate formation pressures in aqueous sodium chloride solutions and in the presence of 2,2-dimethyl butane (neohexane). It is shown that sodium chloride acts as an inhibitor. Earlier experiments have also shown inhibiting action by sodium chloride in structure H hydrate forming systems⁹⁾. In addition equilibrium hydrate formation data for the methane-polypropylene glycol-sodium chloride-water system are reported. This system partially simulates a water based drilling fluid. Water based drilling fluids are the most frequently encountered systems in industry because environmental constraints normally dictate the use of such fluids as opposed to oil based ones¹⁰⁾.

2. Experimental Apparatus and Procedure

The objective of an experiment is to determine the minimum pressure, at a given temperature, where hydrate crystals can co-exist in equilibrium with the fluid phases by following the isothermal pressure search method. A schematic of the equipment is shown in Figure 1. A detailed description of the apparatus and the procedure is given elsewhere^{8,11)}. During the experiment a gaseous mixture of methane and carbon dioxide or a pure methane gas with polypropylene glycol is brought into contact with the water in a high-pressure vessel. In the experiments with neohexane a liquid neohexane-rich phase is also present. In the experiments with neohexane 70 mL of neohexane and 80 mL of water are added into the vessel. It should be noted that in the experiments with glycol and NaCl, it was not possible to dissolve more than 5 wt % NaCl in a solution containing glycol and water in equal proportions. The concentration of 5 wt % was found by trial and error from a starting concentration of 20 wt %.

The heart of the apparatus is a high-pressure equilibrium cell, a 316 stainless steel vessel that is immersed in a temperature-controlled bath. The cell has two circular viewing windows on to the front and back. Mixing of the cell contents is accomplished using a magnetic stir bar that is magnetically coupled to a set of two rotating magnets (Tormag Engineering, Vancouver, B.C.) placed directly underneath the cell. The set of magnets is driven by an electric motor. The temperature at the top, middle and near the bottom inside the cell is measured by three Omega copper-constantan

Figure 1. Gas Hydrate Equilibrium Apparatus

thermocouples with a ± 0.10 K accuracy. The pressure is measured by a Bourdon tube Heisse pressure gauge with a range of 0-14 000 kPa and an accuracy that is believed to be less than 0.25 percent of the span. The composition of the gas phase in the equilibrium cell is analyzed with the usage of a Varian CX 3400 Gas Chromatograph connected on-line with the equilibrium cell and automated with a PC.

3. Results and Discussion

Figure 2 shows the hydrate equilibrium measurements for the 50-50 methane-carbon dioxide mixture in pure water, in a neohexane-containing system and in systems containing sodium chloride. The data in the presence of sodium chloride are also given in Table 1. The other data can be found in the literature⁸. As seen from the data, at temperatures greater than approximately 277.5 K the hydrate formation conditions in the presence of neohexane are in the vicinity of those in pure water. This has been interpreted as structure I hydrate formation whereas the data below 277.5 K as structure H formation⁸. The data in aqueous solution containing sodium chloride in a system with or without neohexane indicate that the salt has an inhibiting effect. The salt causes the hydrate to form at higher pressures at a

Figure 2. Incipient gas hydrate formation conditions from a dry gas mixture containing 50 mole % methane and 50 mole % carbon dioxide, water, neohexane and sodium chloride.

Table 1. Incipient equilibrium hydrate formation conditions data and gas phase molar composition for the methane-carbon dioxide-water-neohexane-sodium chloride system. The concentration of NaCl was 2 wt % in the aqueous phase.

Temperature (K)	Pressure (MPa)	Neohexane	Mole fractions in gas phase	
			CO_2	CH_4
274.2	1.835	present	0.4391	0.5609
275.0	2.035	present	0.4510	0.5490
275.9	2.340	present	0.4598	0.5402
274.1	2.280	not present	0.4725	0.5275
274.9	2.480	not present	0.4779	0.5221
276.2	2.800	not present	0.4821	0.5179

Table 2. Incipient equilibrium hydrate formation conditions data for the methane-polypropylene glycol-sodium chloride-water system.

Temperature (K)	Pressure (MPa)	Polypropylene Glycol (wt %)	NaCl (wt %)
274.8	3.840	50.0	0
276.6	4.260	50.0	0
279.3	5.560	50.0	0
282.0	6.950	50.0	0
283.1	7.820	50.0	0
274.2	4.370	47.5	5.0
276.6	4.940	47.5	5.0
278.2	5.760	47.5	5.0
279.8	6.380	47.5	5.0
282.8	8.475	47.5	5.0

given temperature. This is indication of an inhibiting action that has also been observed in systems with only methane as the light component and four heavier compounds (neohexane, isopentane, adamantane and tert butyl methyl ether⁹).

The incipient hydrate formation conditions for the methane-polypropylene glycol system are given in Table 2 and are shown in Figure 3. Also shown in the figure are data for the methane-pure water system¹⁰. As seen from the figure polypropylene glycol is an inhibitor. This means that hydrates form at higher pressures for a given temperature compared to those in pure water. The glycol is a weaker inhibitor compared to sodium chloride.

Figure 3. The effect of polypropylene glycol and sodium chloride on incipient gas hydrate formation conditions for the methane-water system.

4. Conclusions

Incipient equilibrium hydrate formation pressures for the methane-carbon dioxide-neohexane-sodium chloride-water and methane-polypropylene glycol-sodium chloride-water systems were obtained at different temperatures. The concentration of methane on a water-free basis was 50 % in the methane-carbon dioxide gas mixture. The isothermal pressure search method was employed to locate the minimum pressure at a constant temperature. The results indicated that polypropylene glycol and sodium chloride acted as inhibitors i. e. caused the hydrate to form at a higher pressure at a given temperature compared to the equilibrium hydrate formation pressure in the absence of salt.

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