

# MEASUREMENT OF GAS HYDRATE PHASE EQUILIBRIUM

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## ABSTRACT

Incipient equilibrium hydrate formation conditions for two systems are presented. The isothermal pressure search method was employed. First, structure II hydrate data for the propane-triethylene glycol water system at glycol concentrations of 0, 10 and 20 wt % are given. Triethylene glycol was shown to have considerable inhibiting effect on propane hydrate formation. The other data are hydrate formation conditions for the system methane-carbon dioxide-neohexane-water. The initial gas molar composition on a water-free basis was 80 % methane and 20 % carbon dioxide. At a given temperature, the incipient hydrate formation pressure was found to be within the range of the hydrate formation pressure for the methane-neohexane-water and the carbon dioxide-water systems. Thus, further analysis is required to elucidate the type of hydrate structure.

## INTRODUCTION

During the past five years we have been measuring phase equilibrium data in gas hydrate forming systems in our laboratory. The broad objective of the work is to provide thermodynamic data which will be used either directly in process design of relevant operations in the oil and gas industry or can be used to test the validity of computational methods for phase equilibrium. We have studied the effect of glycols, water soluble polymers and electrolytes in hydrates from natural gas components. In the present work, we provide measurements for two systems: First, phase equilibrium data for the propane-water-triethylene glycol (TEG) system and second data for the methane-carbon dioxide-2,2-dimethyl butane (neohexane) system.

It has been known since the 1930s that natural gas and water can form a solid ice-like compound commonly called gas hydrate (Hammerschmidt, 1934). This may take place at temperatures above the normal freezing point of water. Because the formation of hydrates has severe economic consequences, in oil and gas operations, prevention of formation is major concern. The most common method to prevent hydrate formation is to inject methanol, glycol, or electrolytes (inhibiting substances). There is a growing interest to replace thermodynamic inhibitors with kinetic inhibitors i.e. chemicals which could perhaps prevent the agglomeration of gas hydrates after they have been formed (Muijs, 1991; Sloan et al. 1994; Englezos, 1996). In spite of this growing effort as well as the progress that has been made in hydrate thermodynamics, equilibrium data for gas hydrates are still needed not only for process design but also for the development and testing of predictive methods for hydrate equilibria (Sloan, 1990; Englezos, 1993; Sloan et al. 1994).

Triethylene glycol is an industrially used chemical to inhibit the formation of gas hydrates. Ross and Toczykin (1992) have presented data on the effect of TEG on methane and ethane gas hydrates. These are known to be structure I hydrates. Hence, one of the objectives of this work is to report incipient equilibrium data for propane hydrate in aqueous triethylene glycol solutions. Propane hydrate is known to form structure II type hydrate crystal lattice.

Following the report from the National Research Council (NRC) of Canada in 1987 on a new hydrate structure, Sloan and co-workers reported the first structure H hydrate phase equilibrium data in 1992 (Ripmeester et al. 1987; Ripmeester and Ratcliffe, 1990; Lederhos et al. 1992). The possibility of forming structure H hydrates in gas and oil reservoirs provides the motivation to obtain phase equilibrium data for structure H hydrates. Subsequently, additional data and a method to predict structure H equilibrium were reported from Sloan's laboratory (Lederhos et al. 1993; Mehta and Sloan, 1993; 1994a; Mehta and Sloan, 1994b; Makogon et al. 1996; Mehta and Sloan, 1996). Additional data were also reported by other laboratories (Danesh et al. 1994; Hutz and Englezos, 1996).

Thus far only methane, nitrogen and argon have been used as light components in the formation of structure H hydrates. Carbon dioxide in conjunction with neohexane and ice also forms structure H hydrates (Ripmeester, 1996). In our laboratory, we attempted to prepare such hydrate but in liquid water. However, we were not able to form hydrates which could be of structure H. At a given temperature, the hydrate that was formed was stable at the carbon dioxide structure I hydrate equilibrium pressure.

Hence, we decided to work with a gas mixture of 80 % methane and 20 % carbon dioxide on a molar basis in conjunction with neohexane which serves as the heavy component.

#### APPARATUS AND PROCEDURE

A schematic of the apparatus is shown in Figure 1. It consists of a high pressure 316 stainless steel vessel which is immersed in a temperature controlled bath. It has two circular viewing windows on to the front and back. The top of the vessel is held in place by six stainless steel bolts and is sealed with a neoprene O-ring. The temperature control bath contains 30 L of a solution consisting of approximately 50/50 mass percent water and ethylene glycol. A motor driven mechanism is used to stir the contents of the bath. The temperature of the bath is controlled by an external refrigerator/heater (Forma Scientific model 2095, Caltech Scientific, Richmond, BC) with a capacity of 28.5 L. The refrigerator/heater also uses a 50-50 mass percent glycol-water mixture. 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 thermocouples. Their accuracy is believed to be  $\pm 0.10$  K. The pressure in the cell is measured by a Bourdon tube Heisse pressure gauge from Brian Controls (Burnaby, BC). The range of the gauge is 0-14 000 kPa and its accuracy is believed to be less than 0.25 percent of the span.

The objective of an experiment is to determine the minimum pressure, at a given temperature, where hydrate crystals can co-exist in equilibrium with a gas phase containing mostly propane and the aqueous liquid phase containing the triethylene glycol. In the structure H hydrate formation experiments, the equilibrium is among a gas phase rich in methane and carbon dioxide, an aqueous liquid phase, a liquid hydrocarbon phase rich in neohexane and the hydrate phase. The isothermal pressure search method is used for the determination of the hydrate formation conditions. We use this method because when a pressure change is imposed, the system can reach thermal equilibrium faster compared to the time required for an adjustment of the temperature. More detailed information on the equipment and the procedure to carry out the experiments is available elsewhere (Englezos and Ngan, 1994; Hutz and Englezos, 1996)

The solutions were prepared with deionized water. The purity of methane and propane was 99.9 and 99.5 % (by volume) respectively. These gases as well as the anaerobic grade carbon dioxide were supplied by Medigas. The neohexane (99%) was supplied from Aldrich. Triethylene glycol was also supplied by Aldrich and was 99% pure. The hydrate forming substances were used without any further purification. A Sartorius analytical balance with a readability of 0.05g was used to weigh the compounds used in the experiments.

#### RESULTS AND DISCUSSION

The propane-triethylene glycol-water system. The measured equilibrium hydrate formation conditions are shown in Figure 2 together with the vapour pressure of propane. As seen from the figure, the data indicate an inhibiting effect by TEG on propane hydrate equilibrium. One can read from the graph the hydrate point depression at a given pressure. For example at 300 kPa the hydrate point depression is 1.65 and 3.15 K for the 10 and 20 wt % TEG solutions respectively. At 400 kPa pressure, the hydrate point depressions are 1.70 and 3.25 K for the 10 and 20 wt % solutions respectively. It is noted that the freezing point depressions for these TEG solutions is 1.33 and 2.93 K. Comparing these values with our previous work with glycerol we note that, the inhibiting effectiveness of TEG is therefore comparable to glycerol but less than that of methanol and NaCl on the same weight % basis (Breland and Englezos, 1996). It is also noted that the difference in hydrate point depression for TEG solutions at different pressures are less than experimental uncertainty. Hence, it is assumed that the hydrate point depression values do not depend on pressure.

The methane-carbon dioxide-neohexane-water system. Experiments at NRC showed that carbon dioxide with neohexane forms structure H hydrate (Ripmeester, 1996). In spite of efforts to nucleate such hydrates but in liquid water and not in ice as was done at NRC, we were not able to obtain hydrates of structure H. The hydrate we obtained was stable within the carbon dioxide structure I hydrate equilibrium conditions. Since these experiments were inconclusive, we decided to work with an 80-20 % methane-carbon dioxide-neohexane-water system. Figure 3 shows the hydrate equilibrium measurements. The results indicate that the measured conditions are within the range of the methane-neohexane structure H and the carbon dioxide structure I hydrate formation conditions. At this stage, it is premature to decide upon the structure

of the hydrate. We plan to analyze the gas and the solid phase in order to elucidate the structure.

## CONCLUSIONS

The effect of triethylene glycol (TEG) on the formation of propane hydrate was studied at 0, 10 and 20 wt % aqueous TEG solutions. TEG was found to have a significant inhibiting effect comparable to glycerol but weaker than methanol or NaCl. The experiments with a 80-20 % methane carbon dioxide mixture together with neohexane in liquid water were not conclusive with respect to the structure formed. However, the incipient equilibrium formation conditions for this system were determined.

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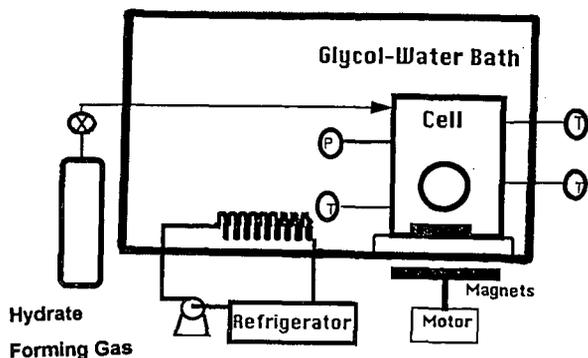


Figure 1. Experimental apparatus

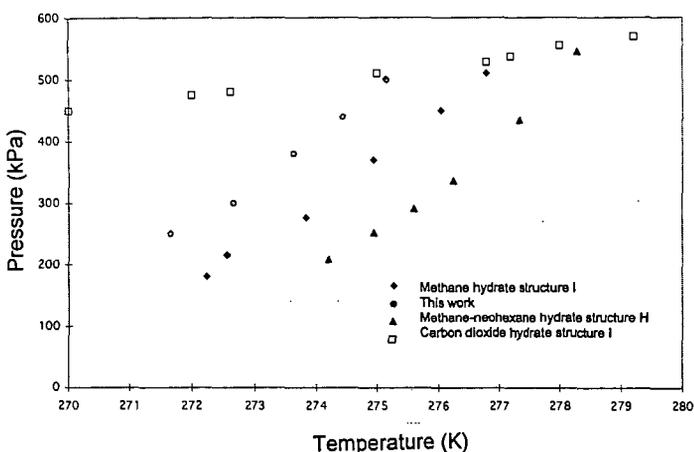


Figure 2. Incipient equilibrium propane hydrate formation conditions in aqueous triethylene glycol solutions.

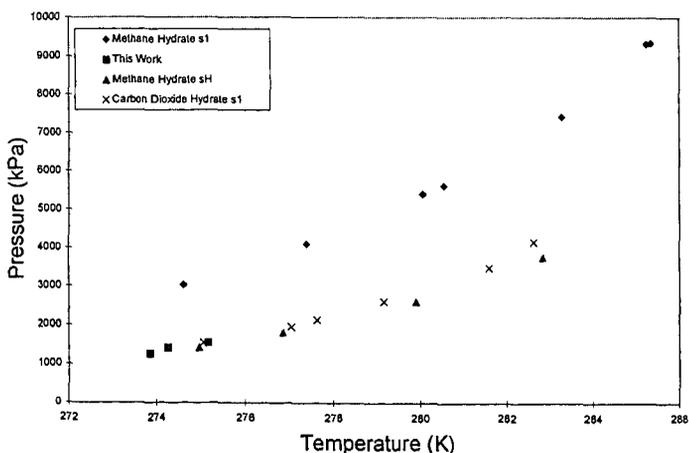


Figure 3. Incipient equilibrium hydrate formation conditions for the methane-carbon dioxide-neohexane-water system.