Incipient Equilibrium Propane Hydrate Formation Conditions in Aqueous Triethylene Glycol Solutions

Phillip Servio and Peter Englezos*

Department of Chemical Engineering, The University of British Columbia, Vancouver, BC V6T 1Z4, Canada

Incipient equilibrium structure II hydrate data for the propane + triethylene glycol (TEG) + water system at glycol concentrations of 10, 20, and 30 mass % in water are reported. The isothermal pressure search method was employed. Experiments were conducted in the temperature range of 270.2 to 276.8 K. Triethylene glycol was shown to have considerable inhibiting effect on propane hydrate formation. However, it was not as effective as an inhibiting agent as sodium chloride or methanol.

Introduction

Measurement of the effect of glycols, water soluble polymers, and electrolytes on the incipient equilibrium gas hydrate formation conditions is necessary for process design. For example, these thermodynamic data can be used directly in the design of operations in the oil and gas industry involving the search, recovery, transport, or processing of hydrocarbon fluids. In addition, they are used to test the validity of computational methods for hydrate phase equilibrium, which will then be used for process design and simulation. Thus, hydrates continue to be of great interest in the hydrocarbon industry for economic and safety reasons. Hydrates are also important in other fields (Sloan, 1990; Englezos, 1993) and have been the subject of two recent international conferences.

The major concern in the hydrocarbon industry is to prevent the formation of hydrates. The classic method for achieving this is the use of inhibiting substances such as alcohols and salts (Sloan, 1990). Triethylene glycol (TEG) is an industrially used chemical to inhibit the formation of gas hydrates. Ross and Toczylkin (1992) have presented data on the effect of TEG on methane and ethane gas hydrates. These are known to be structure I hydrates. The objective of this work is to report incipient equilibrium data for propane hydrate in aqueous triethylene glycol solutions. Propane hydrate is known to form the structure II type hydrate crystal lattice.

Apparatus and Procedure

The apparatus consists of a high-pressure 316 stainless steel vessel that is immersed in a temperature-controlled bath. It has two circular viewing windows on to the front and back. A schematic of the apparatus as well as a detailed description is available elsewhere (Englezos and Ngan, 1994). Mixing of the cell contents is accomplished using a magnetic stir bar that is magnetically coupled to a set of two rotating magnets placed directly underneath the cell. The set of magnets is driven by an electric motor. The temperature at the top, at the middle, and near the bottom inside the cell is measured by three Omega copper-constantan thermocouples. The thermocouples have an accuracy which is believed to be ±0.10 K. The pressure is measured by a Bourdon tube Heisse pressure gauge. The range of the gauge is 0−14000 kPa, and its accuracy is believed to be less than 0.25% of the span.

Table 1. Incipient Equilibrium Data on Propane Hydrate Formation in Aqueous Triethylene Glycol (TEG) Solutions

triethylene glycol (TEG) concn (mass %)	*T*/K	*P*/MPa
10	272.3	0.180
	272.6	0.215
	273.9	0.275
	275.0	0.370
	276.1	0.450
	276.8	0.510
20	271.7	0.250
	272.7	0.300
	273.6	0.380
	274.5	0.440
	275.2	0.500
30	270.2	0.290
	271.5	0.335
	272.4	0.425
	271.0	0.310

The isothermal pressure search method is used for the determination of the hydrate formation conditions (Englezos and Ngan, 1994). 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. The objective of an experiment is to determine the minimum pressure, at a given temperature, where hydrate crystals can coexist in equilibrium with a gas phase containing mostly propane and the aqueous liquid phase containing the triethylene glycol.

The solutions were prepared with deionized water. The purity of propane was 99.5% (volume). The propane was supplied by Medigas. Triethylene glycol was 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 0.05 g was used to weigh the compounds used in the experiments.

Results and Discussion

The measured equilibrium hydrate formation conditions are given in Table 1 and are also shown in Figure 1 together with the vapor pressure of propane and hydrate formation conditions in pure water. The hydrate formation conditions in pure water were reported by Robinson and Mehta (1971) and Englezos and Ngan (1994). 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

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* Author to whom correspondence should be addressed.

S0021-9568(97)00048-4 CCC: $14.00

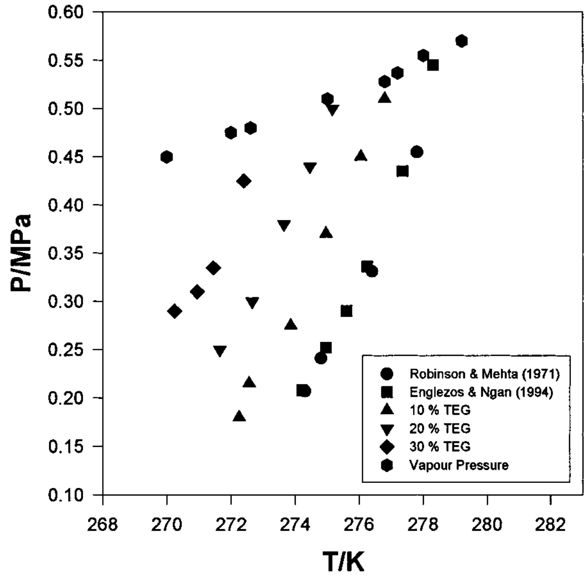

Figure 1. Incipient equilibrium propane hydrate formation conditions in pure water and in aqueous triethylene glycol (TEG) solutions.

1.6 and 3.5 K for the 10 and 20 mass % TEG solutions respectively.

We compared the effect of TEG with the measurements from our previous work with glycerol and the carbon dioxide hydrate (Breland and Englezos, 1996). It was found that the inhibiting effectiveness of TEG is comparable to glycerol at the same weight % basis. The inhibiting effect of triethylene glycol was also compared with that of methanol and NaCl on the same mass % basis. In addition, data for propane hydrate formation in 15 mass % polyethylene oxide (PEO) solutions are included. The above data are shown in Figure 2. The data for the methanol solutions were taken from Ng and Robinson (1983), whereas those for NaCl are taken from Sloan's monograph (Sloan, 1990). The data in PEO solutions were taken from Englezos and Ngan (1994). As seen from the figure, methanol is the strongest inhibiting substance on a weight percent basis, sodium chloride is more effective than TEG, and PEO is a very weak inhibitor.

Conclusions

The effect of triethylene glycol (TEG) on the equilibrium propane hydrate formation conditions was measured. Experiments using TEG concentrations of 10, 20, and 30 mass % in water were conducted. Although TEG was found to have a significant inhibiting effect, it is a weaker inhibitor than sodium chloride and methanol. TEG is an inhibitor equivalent to glycerol.

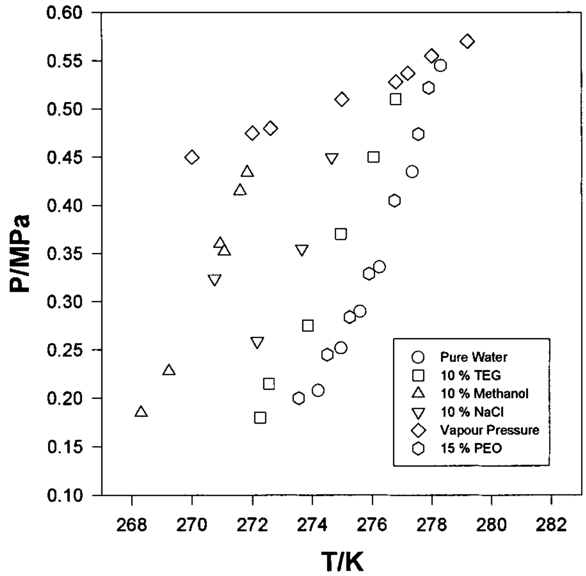

Figure 2. Incipient equilibrium propane hydrate formation conditions in pure water and in aqueous solutions of triethylene glycol (TEG), polyethylene oxide (PEO), NaCl, and methanol.

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Received for review February 24, 1997. Accepted May 1, 1997.® The financial support from the Natural Sciences and Engineering Research Council of Canada (NSERC) and the Science Council of British Columbia (SCBC) is greatly appreciated.

JE9700481

® Abstract published in *Advance ACS Abstracts,* June 15, 1997.