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Equilibrium Hydrate Formation Data for Carbon Dioxide in Aqueous Glycerol Solutions

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Equilibrium conditions for carbon dioxide hydrate in pure water and aqueous glycerol solutions were measured in order to evaluate the effectiveness of glycerol as an inhibiting agent. The isothermal pressure search method was employed. Twenty-two experiments were conducted in the temperature range of 270.1−280.2 K using glycerol concentrations of 0, 10, 20, and 30 mass % in water. Glycerol was shown to have a considerable inhibiting effect on carbon dioxide hydrate formation though it was not as effective as an inhibiting agent as sodium chloride or methanol.

Introduction

Carbon dioxide hydrate is a solid solution of water and carbon dioxide. Carbon dioxide hydrate is a clathrate compound also known as gas hydrate. Clathrates are inclusion compounds which are formed as a result of physical interactions between two molecular species. One species (host) forms a lattice which physically traps the other species (guest). No chemical bonds are formed between the host molecules and the guest molecules. The carbon dioxide + water system will form clathrate or gas hydrate at certain temperature and pressure conditions. The term hydrate refers to the presence of water as the host species. The ability of water to form clathrate compounds is due to the hydrogen bonding of water molecules. There are more than 100 chemicals which can form clathrate hydrates. Information on the structure, physical and thermodynamic properties, and technological significance of gas hydrates is available in several publications (Sloan, 1990; Englezos, 1993; Sloan et al., 1994).

It has been known since the 1930s that natural gas and water can form gas hydrate at temperatures above the normal freezing point of water and thus plug a pipeline that is used for gas transport (Hammerschmidt, 1934). Because the formation of hydrates has severe economic consequences, prevention of formation is therefore a major concern. One of the techniques to prevent hydrate formation is to alter the partial phase diagram of the gas−water system in the hydrating region by injecting methanol, glycol, or electrolytes (inhibiting substances). Methanol and glycol injections are used extensively in gas and oil systems.

Incipient equilibrium data and predictive methods for gas hydrates are needed for the design of the facilities that deal with mixtures capable of forming hydrates. Data are also needed for the development and testing of predictive methods for hydrate equilibria. Incipient equilibrium data for carbon dioxide hydrate in aqueous glycerol solutions are needed for the design of facilities that use carbon dioxide in miscible flooding (Blytas, 1987). The CO_2 used in enhanced oil recovery is produced from underground formations in which it occurs saturated with water. This water must be removed in order to avoid formation of carbon dioxide hydrate in the pipeline that carries it from the point of production to the points of injection. Hydrate formation must also be inhibited at the CO_2 production site from the point of production to the point of dehydration. Prevention of hydrate formation can be accomplished by using ethylene glycol, glycerol, diethyl glycol, or triethyl glycol. It is noted that when diethyl or triethyl glycol is used in the drying of carbon dioxide high losses are encountered due to the solubilization in the compressed CO_2. Thus, the use of glycerol is advantageous because it leads to lower solubility losses. Glycerol is also used in water-based drilling fluid formulations (Bland, 1991) and is considered an environmentally less hazardous compound than methanol and glycol at offshore platforms (Ng and Robinson, 1994). Ng and Robinson (1994) reported three measurements of hydrate−vapor CO_2−liquid water equilibrium and two measurements of hydrate−liquid CO_2−liquid water equilibrium. The concentration of glycerol was 25 mass %. The objective of this work is to report additional incipient equilibrium data for carbon dioxide hydrate in aqueous glycerol solutions. Solutions with glycerol concentrations of 10, 20, and 30 mass % were studied.

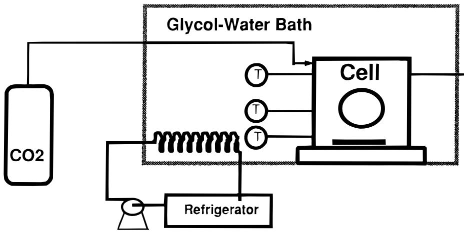

Figure 1. Schematic of the apparatus.

Apparatus

A schematic of the apparatus to be used in this experiment appears in Figure 1. The apparatus is described in detail by Englezos and Ngan (1994). A high-pressure cell is immersed in a temperature-controlled bath. The cell was constructed from a 316 stainless steel rod. Two circular viewing windows were fitted onto the front and back. The top of the cell can be removed and is held in place by six stainless steel bolts. The top is sealed with a neoprene O-ring. The temperature control bath contains 30 L of a solution consisting of approximately 50/50 (mass %) 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, British

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Table 1. Incipient Equilibrium Data on CO_2 Hydrate Formation in Aqueous Glycerol Solutions

glycerol mass percent	*T*/K	*P*/MPa	glycerol mass percent	*T*/K	*P*/MPa
0	275.5	1.651	20	270.4	1.502
	276.8	1.936		270.6	1.556
	280.2	3.021		272.3	1.776
10	272.3	1.391		273.6	2.096
	274.6	1.786		274.1	2.281
	276.1	2.191		275.5	2.721
	277.7	2.640		276.2	3.001
	278.4	2.942		277.1	3.556
	279.3	3.345	30	270.1	2.030
				270.6	2.096
				271.4	2.34
				272.3	2.651
				273.2	2.981

Columbia) with a capacity of 28.5 L. The refrigerator/heater also uses a 50/50 (mass %) 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, British Columbia) placed directly underneath the cell. The set of magnets is driven by an electric motor. The temperature inside the cell is measured using three copper−constantan thermocouples supplied by Omega. The thermocouples are placed evenly throughout the cell with one near the top, one at the middle, and one near the bottom. The accuracy of the thermocouples is believed to be ±0.10 K. The pressure in the cell is measured using a Bourdon tube Heisse pressure gauge from Brian Controls (Burnaby, British Columbia). The range of the pressure gauge is 0−14 000 kPa. The accuracy of the pressure measurements is believed to be less than 0.25% of the span.

Procedure

Incipient equilibrium measurements for clathrate hydrate formation in the water−carbon dioxide−glycerol system were taken. The objective of an experiment was to measure the pressure, at a given temperature, where hydrate crystals can coexist in equilibrium with a gas phase containing mostly carbon dioxide and the aqueous liquid phase. According to the phase rule, this is a unique pressure.

Glycerol is completely miscible in water, so only one liquid phase was present throughout the experiment. The glycerol was supplied by Fisher Chemicals and was 99.5% pure. The anaerobic grade carbon dioxide used was supplied by Medigas. Four different concentrations of glycerol measured in mass percent in water were tested. The concentrations of glycerol tested were 0, 10, 20, and 30 mass %. A series of experiments using a glycerol concentration of zero was conducted and the results compared to published data for water−carbon dioxide. This procedure ensured that the experimental technique used in this study would give results consistent with those from other works.

Before starting the measurements of the incipient formation pressures at different temperatures using a particular glycerol solution, hydrate formation tests were performed in order to eliminate the hysteresis phenomenon associated with hydrate formation. The high-pressure cell was cleaned thoroughly, and 125 mL of the solution of water and glycerol was injected into the cell. The cell was sealed and mixing of the solution commenced. The cell was pressurized and then purged with carbon dioxide three times to ensure pure carbon dioxide was the atmosphere within the cell. Perhaps a small amount of air remained in the Bourdon tube, but it was assumed that it would not affect the measurements. A temperature was chosen and was controlled by the refrigeration unit and ethylene glycol−water bath. Once the system was at constant temperature, the cell was pressurized with carbon dioxide to a pressure that results in a large amount of hydrate forming. The pressure was decreased to below the equilibrium point, and the hydrate was allowed to decompose. This procedure was repeated two or three times per solution tested.

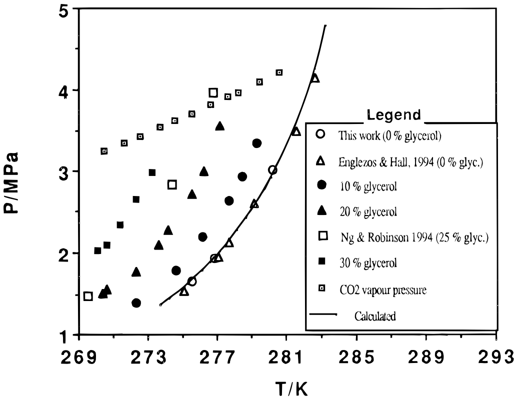

Figure 2. Equilibrium data on carbon dioxide hydrate formation in water−glycerol.

After the completion of the preliminary formation tests, the measurement of the incipient hydrate formation pressure was carried out at different temperatures following the *isothermal pressure search* procedure. That procedure is described in detail elsewhere (Englezos and Bishnoi, 1991; Englezos and Ngan, 1994).

Results and Discussion

The measured equilibrium hydrate formation conditions are given in Table 1. The data are also plotted and shown in Figure 2 in order to show the magnitude of the inhibitive effect of glycerol on the formation of carbon dioxide hydrate crystals. Experiments were conducted with the pure water−carbon dioxide system first to ensure the results obtained during these experiments would be consistent with those from the work of others. These results are indicated in the legend as 0% glycerol. Figure 2 shows that these results are in good agreement with those obtained earlier by Englezos and Hall (1994) who compared their results with those from five other sources and found all in very good agreement.

Experiments were conducted with aqueous solutions of 10, 20, and 30 mass % glycerol, and the results are shown in Figure 2. Higher concentrations were not tested because the range of temperatures where experiments could be conducted was limited by two factors. Temperatures were limited on the low side since the apparatus could achieve a minimum temperature of 270 K. Temperatures were limited on the high side because of the carbon dioxide vapor pressure. The results by Ng and Robinson (1994) at 25 mass % glycerol are also shown in Figure 2. As seen they indicate an inhibiting action with a strength that is between that of the 20 and 30 mass % solutions. Interestingly, the point at the highest pressure appears to be above that at the carbon dioxide vapor pressure.

Table 2 shows the hydrate point depression for each concentration at three different pressures, and these values are compared to the freezing point depression values of aqueous glycerol solutions (*CRC Handbook*, 51st ed.). Since there are no data for hydrate point depression values at atmospheric pressure, a strictly direct comparison could not be made. However, the differences in hydrate point depression for aqueous glycerol solutions at different

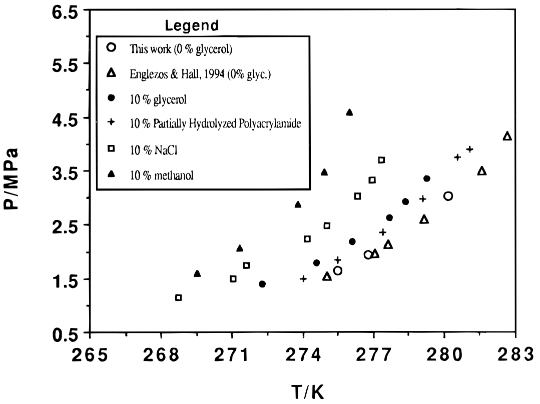

Figure 3. Comparison of inhibitive effects of varying agents on the equilibrium carbon dioxide hydrate formation conditions.

Table 2. Freezing Point Depression (ΔT), Hydrate Point Depression (ΔT_H), and Change in Hydrate Point Depression at 2000 kPa ($\Delta T_{H,2000}$) in Glycerol−Water

glycerol mass percent	ΔT/K	ΔT_H/K			$\Delta T_{H,2000}$/K
	$P = 101.3$ kPa	$P = 2000$ kPa	$P = 2500$ kPa	$P = 3000$ kPa	$P = 2000$ kPa
0	0	0	0	0	
10	2.323	1.66	1.68	1.72	1.66
20	5.46	4.03	4.13	4.09	2.37
30	9.76	6.82	7.06	7.12	2.79

pressures are less than the experimental uncertainty, so it was assumed that the hydrate point depression values are insignificantly affected by pressure.

Table 2 also shows the change in hydrate point depression for increasing concentrations of glycerol at 2000 kPa. The effect of adding more glycerol is nonlinear as is the effect of glycerol on the freezing point depression. In dilute solutions, an assumption is made that the freezing point depression is directly related to concentration by the cryoscopic constant, resulting in a linear relation of concentration to freezing point depression. At higher concentrations this assumption is not valid. The data suggest that the hydrate point depression may behave in a similar manner.

Figure 3 compares the inhibitive effects of glycerol on hydrate crystal formation to that of other substances. Aqueous solutions of 10 mass % methanol, sodium chloride, or glycerol and 90% partially hydrolyzed polyacrylamide (PHPA) were compared. The data for the methanol solutions were taken from Ng and Robinson (1983) whereas those for sodium chloride and PHPA solutions were taken from Englezos and Hall (1994). The figure shows that methanol is the strongest inhibiting substance on a weight percent basis, sodium chloride is more effective than glycerol, and PHPA is the weakest inhibitor.

Other observations made during the experiment were as follows. Clathrate hydrate crystal formation was influenced by the difference between the equilibrium pressure and the actual pressure. A larger pressure difference provided a larger driving force for crystal formation, and nucleation occurred quicker. Though crystal nucleation was sometimes slow, crystal formation was fast once nucleation occurred.

Conclusion

The effect of glycerol on the formation of carbon dioxide clathrate hydrates was studied. Experimental results of the inhibitive effect of glycerol were presented in this paper. Glycerol was found to have a significant inhibitive effect. Glycerol is a stronger inhibitor than partially hydrolyzed polyacrylamide but weaker than sodium chloride and methanol.

Literature Cited

Bland, R. Development of New Water Based Mud Formulations. In *Chemicals in the Oil Industry: Developments and Applications*; Ogden, P. H., Ed.; Royal Society of Chemistry: London, 1991; pp 83−98.

Blytas, G. C. Separations Technology in the Oil Industry of the 80's and 90's. In *Separation Technology*, Proceedings of the Engineering Foundation Conference, Schloss Elmau, Bavaria, West Germany, April 27−May 1, 1987; Li, N. N., Strathmann, H., Eds.; American Institute of Chemical Engineers: New York, 1988.

Englezos, P. Clathrate Hydrates. *Ind. Eng. Chem. Res.* **1993**, *32*, 1251−1274.

Englezos, P.; Bishnoi, P. R. *Ind. Eng. Chem. Res.* **1991**, *30*, 1655−1659.

Englezos, P.; Hall, S. *Can. J. Chem. Eng.* **1994**, *72*, 887−893.

Englezos, P.; Ngan, Y. T. *Fluid Phase Equilib.* **1994**, *92*, 271−288.

Hammerschmidt, E. G. *Ind. Eng. Chem.* **1934**, *26* (8), 851−855.

Ng, H.-J.; Robinson, D. B. In *Annals of the New York Academy of Sciences*; Sloan, E. D., Happel, J., Hnatow, M. A., Eds.; New York Academy of Sciences: New York, 1994; Vol. 715, pp 450−462.

Ng, H.-J.; Robinson, D. B. Research Report RR-66; Gas Processors Association. Tulsa, OK, 1983.

Sloan, E. D., Jr. *Clathrate Hydrates of Natural Gases*; Marcel Dekker, Inc.: New York, 1990.

Sloan, E. D.; Happel, J.; Hnatow, M. A. International Conference on Natural Gas Hydrates. *Ann. N. Y. Acad. Sci.* **1994**, *715*.

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