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Inhibiting Effect of Triethylene Glycol and Glycerol on Gas Hydrate Formation Conditions

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The effect of triethylene glycol and glycerol on the equilibrium hydrate formation conditions from methane (91 mol %) + ethane and methane (90.5 mol %) + propane mixtures was determined. Aqueous solutions containing (20 and 30) wt % triethylene glycol and 20 % glycerol were tested. The data showed that both chemicals have considerable inhibiting effect on hydrate formation and that the inhibiting effect is proportional to the inhibitor concentration.

Introduction

The formation of gas hydrates is known to be a serious problem in the gas and oil industry since it may result in plugging of the pipelines or other processing equipment.[1] The addition of chemicals known as thermodynamic inhibitors in the water phase to prevent hydrate formation is a general method used in the oil and gas industry. Commonly used inhibitors are methanol, ethylene glycol (EG), glycerol, and triethylene glycol (TEG). Knowledge of the equilibrium hydrate-forming conditions is necessary for the rational and economic design of processes in the chemical, oil, and other industries where hydrate formation is encountered.[2] In addition, equilibrium hydrate formation data are also valuable for validating the hydrate prediction models.

The thermodynamics of hydrate formation have been studied extensively over many years, and data for several thermodynamic inhibitors have been obtained. However, the data for some specific inhibitors, such as TEG and glycerol, are not adequate. Ross and Toczylkin[3] have presented data on the effect of TEG on methane and ethane gas hydrates. Servio and Englezos[4] measured incipient equilibrium propane hydrates formation conditions in aqueous TEG solution. TEG was shown to have considerable inhibiting effect on propane hydrate formation. Breland and Englezos[5] measured the equilibrium hydrate formation data for carbon dioxide in aqueous glycerol solutions. It was shown that the inhibiting effectiveness of TEG is comparable to glycerol at the same wt % basis but that both inhibitors are weaker than methanol. The objective of this work was to measure the incipient equilibrium hydrate formation data for methane + ethane and methane + propane hydrates in the presence of TEG and glycerol.

Experimental Section

Apparatus and Procedure. The apparatus, shown in Figure 1, consists of the equilibrium cell (C), which is immersed in a temperature-controlled bath. The liquid in the bath is a 50/50 wt % mixture of water and ethylene glycol. The temperature of the glycol/water mixture is controlled by an external refrigerator/heater (VWR Scientific, model 1187). A relatively constant temperature (± 0.10 K) in the bath over a long period of time is maintained. The equilibrium cell is made from plexiglass. The inside diameter is 25 mm, and the height is 44 mm. The thickness of the cell wall is 6 mm. This column has stainless steel lids on both sides that are held in place by three stainless steel bolts. Four neoprene O-rings were used to seal the lids. Stirring of the cell contents is accomplished by using a magnetic stir bar coupled to a set of magnets underneath the equilibrium cell. The temperature inside the cell is measured with a copper-constant thermocouple from Omega that is placed just below the liquid−gas interface surface. The temperature is believed to be known within ± 0.1 K. The pressure is measured by a HEISE digital pressure indictor, which is calibrated by an accurate pressure gauge (WIKA 27888DA). The uncertainty of the pressure measurements is ± 50 kPa. Samples can be obtained from the gas phase of the equilibrium cell. The composition of the samples is obtained by gas chromatography (GC) (Varian CX3400). The hydrate formation and decomposition process can be observed through the microscope (Nikon, SMZ-2T), which is situated in front of the water bath. It provides more accurate observation with 5× magnification.

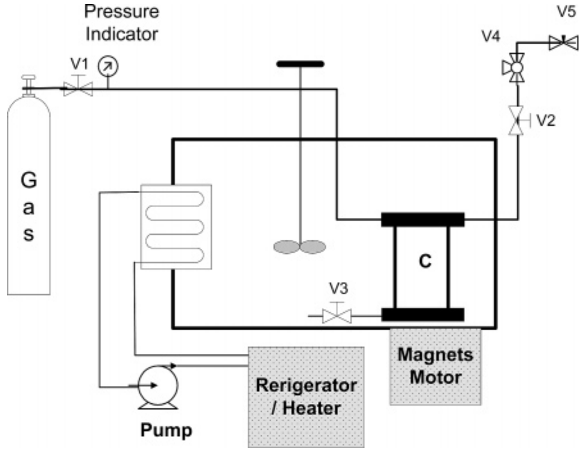

Figure 1. Apparatus: C, equilibrium cell; V1, V2, V3, V4, V5, valves.

Aqueous inhibitor (TEG or glycerol) solutions were prepared by adding an appropriate amount of inhibitor in water to achieve a desired inhibitor concentration. In particular solutions containing (20.2, 20.0, and 30.0) wt % triethylene glycol and 20.0 wt

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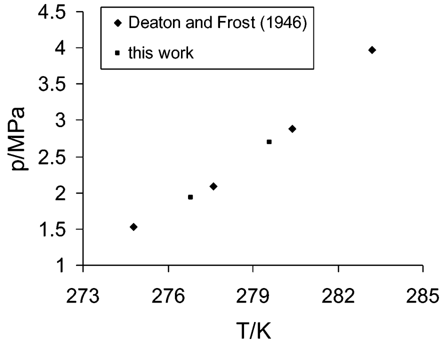

Figure 2. Methane + ethane equilibrium hydrate formation data.

% glycerol were needed. It is noted that triethylene glycol and glycerol are all miscible with water in all proportions at room temperature. The appropriate amounts of laboratory grade TEG or glycerol and deionized water were weighed using a Mettler P2000 balance with readability of 0.1 mg. The solutions were added into the equilibrium cell, stirred for 30 min for complete mixing, and held until the desired temperature was reached.

Each measurement consists of finding the pressure at a constant temperature at which an infinitesimal amount of hydrate crystals exists in equilibrium with the aqueous and the hydrocarbon vapor phases. These are the incipient equilibrium conditions. Practically, this is the situation when a small number of very tiny crystals (visible by a microscope) coexist in equilibrium with the fluid phases. The isothermal pressure search method is used for the determination of the hydrate formation.[6] This method is used because the system can reach thermal equilibrium faster as compared to the time required for an adjustment of the temperature.

Deionized water was used to avoid the contamination of unwanted salt during the experiments. TEG was obtained form Sigma-Aldrich Canada, Ltd. The purity was 99 %. Glycerol with 99.7 % purity was obtained from Fisher Scientific. During the experiments, 20.0 % and 30 % (by weight) TEG solution and 20.0 % glycerol solution were used. The dry gas composition of the $CH_4 + C_2H_6$ (C1 + C2) mixture and the $CH_4 + C_3H_8$ (C1 + C3) mixture from cylinders were determined by gas chromatography prior to starting the experiments. The methane content was found to be 91.0 mol %, and the balance of ethane was in the C1 + C2 gas cylinder. The methane content of the C1 + C3 cylinder was 90.5 mol %, and the balance was propane.

Results and Discussion

Prior to the experiments, two equilibrium data for methane hydrate formation were obtained at (274.0 and 280.4) K and compared with values from the literature. The measured incipient hydrate formations pressures were (2.94 and 5.53) MPa, respectively. They are in excellent agreement with other data as one may easily verify since data for methane hydrate are widely available.[1]

In addition, we compared our data for the methane + ethane + water system with data from the literature,[7] which were obtained for a binary methane + ethane system with 90.4 mol % methane, which is close to the 91 % methane content in our mixture. The results are shown in Figure 2. As seen, the results from our apparatus compare very well with literature values.

Table 1. Incipient Equilibrium Hydrate Formation Pressure and Gas Phase Molar Composition for the $CH_4 + C_2H_6$ + TEG + H_2O Hydrate Formation System

	T	*P*	gas-phase mole fraction	
inhibitor and its concentration	K	MPa	CH_4	C_2H_6
0	279.6	2.700		
	276.8	1.928		
TEG (20.2 wt %)	282.0	4.458	91.4	8.6
	280.8	3.858	91.4	8.6
	279.5	3.280		
	276.5	2.430	91.4	8.6
	274.9	2.087	91.4	8.6
	272.6	1.528	91.5	8.5
TEG (30.0 wt %)	280.2	4.520		
	279.4	4.130	90.8	9.2
	277.4	3.400	90.7	9.3
	275.3	2.800	90.9	9.1
	273.8	2.280	90.9	9.1

Table 2. Incipient Equilibrium Hydrate Formation Pressure and Gas Phase Molar Composition for the $CH_4 + C_3H_8$ + TEG + H_2O Hydrate Formation System

	T	*P*	gas-phase mole fraction	
concentration of TEG (wt %)	K	MPa	CH_4	C_3H_8
0	280.6	1.19		
	278.9	0.99		
	277.0	0.78	90.6	9.4
	275.4	0.65	90.6	9.4
	273.6	0.52	90.4	9.6
20.0	281.4	1.76	91.6	8.4
	279.5	1.42	91.4	8.7
	277.3	1.14	91.6	8.4
	275.4	0.91	90.9	9.1
	273.6	0.75		
30.0	281.7	2.21	90.3	9.7
	280.0	1.83		
	277.8	1.39	90.1	9.9
	276.0	1.12	90.5	9.5
	274.2	0.9		

Table 3. Incipient Equilibrium Hydrate Formation Pressure and Gas Phase Molar Composition for the $CH_4 + C_2H_6$ + Glycerol + H_2O Hydrate Formation System

	T	*P*	gas-phase mole fraction	
concentration of glycerol (wt %)	K	MPa	CH_4	C_2H_6
20	274.2	2.130	90.9	9.1
	276.3	2.620	91.1	8.9
	278.8	3.420	90.8	9.2
	280.1	4.100		
	281.3	4.751	90.8	9.2

Table 4. Incipient Equilibrium Hydrate Formation Pressure and Gas Phase Molar Composition for the $CH_4 + C_3H_8$ + Glycerol + H_2O Hydrate Formation System

	T	*P*	gas-phase mole fraction	
concentration of glycerol (mass %)	K	MPa	CH_4	C_3H_8
20	274.2	0.870	90.0	10.0
	275.7	1.020	90.0	10.0
	278.3	1.330	90.1	9.9
	280.3	1.690	90.1	9.9
	281.6	1.990		

The effect of TEG on the incipient equilibrium conditions for methane + ethane and methane + propane hydrate formation is shown in Tables 1 and 2, respectively. As seen, the inhibiting effect of TEG is considerable and increases with concentration. In addition, the gas compositions in equilibrium conditions measured using GC are also given. As seen, the methane concentration is slightly above the dry gas composition of the cylinder and that of propane is slightly below. Considering that the amount of hydrate is infinitesimal, the gas-phase compositions reflect the fact that there is a differential solubility of these hydrocarbons in water. Tables 3 and 4 show the results with

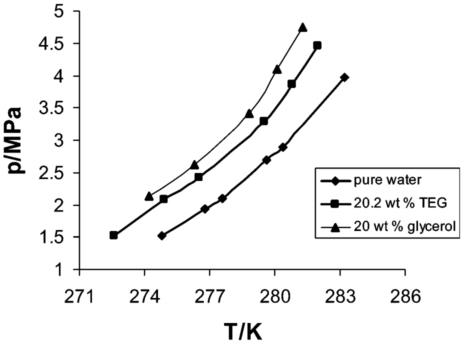

Figure 3. Equilibrium data on methane + ethane hydrate formation in water and in aqueous triethylene glycol and glycerol solutions.

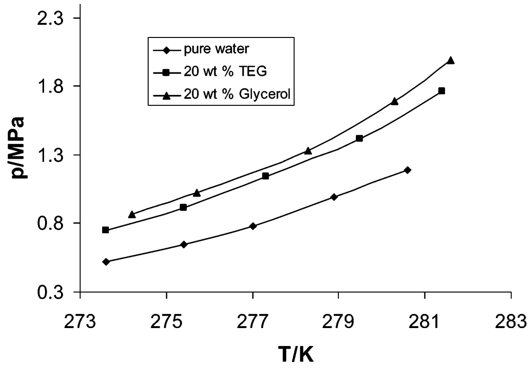

Figure 4. Equilibrium data on methane + propane hydrate formation in water and in aqueous triethylene glycol and glycerol solutions.

the inhibiting effect of glycerol on the hydrate formation conditions for the two binary hydrocarbon mixtures along with the gas-phase compositions at equilibrium. As seen, glycerol also has a considerable inhibiting effect in hydrate formation. A noteworthy property of the CH_4 + C_2H_6 system is that although CH_4 and C_2H_6 are known to form structure I hydrate, the binary gas mixture may form structure II hydrate at certain compositions and temperatures.[8−10]

A measure of the relative inhibiting ability is obtained from the plots of the tabulated pressure−temperature equilibrium data. Figure 3 shows the effect of TEG and glycerol on the equilibrium hydrate formation conditions from methane + ethane and methane + propane, respectively. The plot illustrates graphically the inhibiting effect. In addition, the results indicate that at almost the same wt % inhibitor concentration the effect of glycerol is more pronounced (e.g., this is a stronger inhibitor). Figure 4 shows similar results for the methane + propane system. Again the glycerol is found to be a stronger inhibitor than triethylene glycol. Among the commonly used organic chemicals as inhibitors, methanol is known to be the strongest, but process conditions sometimes necessitate the use of glycols or glycerol.[1]

Conclusions

TEG and glycerol are common thermodynamic inhibitors used in the gas and oil industry. In this work, their inhibiting effect on gas hydrate formation from methane (91 mol %) + ethane and methane (90.5 mol %) + propane mixtures was determined. The concentrations of the TEG in the water phase were (20 and 30) wt % whereas that of glycerol was 20 wt %. Both chemicals were found to have a significant inhibiting effect that is proportional to their concentration in the water. Finally, glycerol was found to be a stronger inhibitor than TEG.

Acknowledgment

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