

Equilibrium Hydrate Formation Conditions for Hydrogen Sulfide, Carbon Dioxide, and Ethane in Aqueous Solutions of Ethylene Glycol and Sodium Chloride

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Incipient equilibrium hydrate formation conditions for hydrogen sulfide, carbon dioxide, and ethane in aqueous solutions of ethylene glycol and sodium chloride were experimentally obtained in the temperature range 264–290 K and the pressure range 0.23–3.18 MPa. A variable-volume sapphire cell was used for the measurements.

Introduction

Natural gas components such as hydrogen sulfide, carbon dioxide, and ethane form gas hydrates of structure I under suitable temperature and pressure conditions. Information on such conditions is vital to the oil and gas industry in order to design and operate processing equipment and pipelines so that hydrate formation is avoided. Development of thermodynamic methods to calculate the hydrate equilibrium conditions requires accurate experimental data.

Ethylene glycol and electrolytes are known as gas hydrate inhibitors. Even though ethylene glycol has been used as an inhibitor for many years by the petroleum industry, there are only a few studies reported (Ng et al., 1985; Robinson, Ng, 1986; Song, Kobayashi, 1989) involving ethylene glycol and natural gas or its individual components in the open literature.

In the present work experimental three-phase (aqueous liquid solution, vapor, and incipient solid hydrate) equilibrium data for hydrogen sulfide, carbon dioxide, and ethane in the presence of aqueous solutions of ethylene glycol and sodium chloride are reported. The measurements are made in the temperature range 264–290 K and the pressure range 0.23–3.18 MPa.

Experimental Setup and Procedure

The equilibrium cell and experimental setup and procedure used for obtaining the data are similar to those described by Dholabhai et al. (1997) and Mahadev and Bishnoi (1999). The equilibrium cell is a “full view” sapphire variable-volume cell with a movable piston. The cell consists of top and bottom flanges which hold a sapphire tube and have ports for charging the solution, thermocouples for temperature measurements, gas inlet/pressure measurement, and vapor-phase sampling. Its schematic and mechanical details are described by Dholabhai et al. (1997) and Parent (1993).

The equilibrium cell is immersed in a constant-temperature bath. A refrigerated ethylene glycol–water solution is used as the circulating coolant. The cell contents are mixed by a stir bar, which is coupled with a rotating

magnet mounted on a shaft of a motor located underneath the cell. The cell pressure is measured using a pressure gauge and a differential pressure transmitter (DP). The low-pressure side of the DP is open to the atmosphere. The DP is calibrated against a dead weight tester. The span of the DP is 11 MPa with a combined accuracy of 0.25% of the span (i.e. 28 kPa). The temperatures are measured with thermocouples calibrated against a standard probe in the range 264–290 K with the standard deviation of the least-squares fit of 0.12 K. The signals from the thermocouples and the DP are acquired by a data acquisition system driven by a personal computer (PC). The pressure and temperature data from the acquisition system are saved at preset sampling intervals on a computer storage disk. The set point of the temperature controller on the refrigerated bath can be changed in multiples of 0.1 K. The temperature in the cell generally oscillates within 0.1 K during a 24 h period. The schematic of the apparatus is given by Dholabhai et al. (1997) and Mahadev and Bishnoi (1999).

The cell is rinsed with deionized-and-distilled water and the experimental solution. The cell is repeatedly flushed with the gas from the cylinder. A gas sample from the cell is analyzed on a gas chromatograph (GC) to ensure the absence of air. About 12 mL of the solution is then charged into the cell, and the vent is closed. Generally, four experiments are performed at increasing temperatures for each solution.

The experimental data for the different systems are obtained using the “pressure search” procedure (Bishnoi and Dholabhai, 1993). The presence of hydrates in the solution is detected visually in the equilibrium cell. Once the solution in the cell reaches the desired temperature, the pressure in the cell is raised sufficiently above the estimated equilibrium pressure. The hydrates are allowed to form, and then the pressure is lowered by moving the cell piston to decompose the hydrates. The procedure is repeated once more. Then the hydrates are formed again, and the equilibrium pressure is established using the pressure search method. The steady pressure and temperature at which a small quantity of the hydrates remain stable for an extended period of time (3–4 h) are taken as the equilibrium condition. The pressure in the cell is lowered by 50 kPa to confirm that all the hydrates

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Table 1. Composition of the Aqueous Solutions

solution ID	ethylene glycol mass % ^a	NaCl mass % ^a
EG30-1	29.96	
EG15-1	14.99	
EG15Na10-1	15.00	9.90
EG15-2	15.07	
EG15Na10-2	15.08	10.02
EG10Na10	10.00	10.05
EG10Na15	10.00	15.00
EG15-3	14.99	
EG30-3	30.00	
EG30-2	30.00	

^a The mass % values are on a wet basis.

Table 2. Experimental Hydrate Equilibrium Conditions for Hydrogen Sulfide in Aqueous Solutions of Ethylene Glycol and Sodium Chloride

solution ID	T/K	P/MPa
EG30-1	272.99	0.23
	277.72	0.39
	281.79	0.61
	285.69	0.92
	289.92	1.50
EG15-1	276.93	0.22
	281.18	0.32
	284.99	0.48
	291.13	0.90
	295.07	1.44
EG15Na10-1	273.59	0.27
	279.26	0.47
	284.93	0.88
	287.23	1.14
	289.38	1.46

Table 3. Experimental Hydrate Equilibrium Conditions for Carbon Dioxide in Aqueous Solutions of Ethylene Glycol and Sodium Chloride

solution ID	T/K	P/MPa
EG15-2	268.24	1.06
	270.36	1.37
	272.87	1.88
	274.90	2.50
	276.65	3.14
EG15Na10-2	265.95	1.66
	267.92	2.17
	269.42	2.89
EG10Na10	266.86	1.39
	268.60	1.71
	269.84	2.16
	271.48	2.72
	272.70	3.18
EG10Na15	264.65	1.83
	265.68	2.15
	266.46	2.35
	267.22	2.67
EG30-2	264.36	1.20
	265.91	1.49
	269.79	2.65

decompose. The temperature of the solution is increased and the procedure is repeated to obtain other equilibrium data.

Experimental Results and Discussion

The compositions of the aqueous solutions studied in this work are shown in Table 1. Experimental three-phase equilibrium data for hydrogen sulfide, carbon dioxide, and ethane in the presence of different aqueous solutions of ethylene glycol and sodium chloride as well as mixtures of ethylene glycol and sodium chloride solutions are given in the Tables 2–4. The results are also presented graphically in Figures 1–3. The solid lines shown in the figures are drawn by “visual fit” to clarify the trends of the data. The

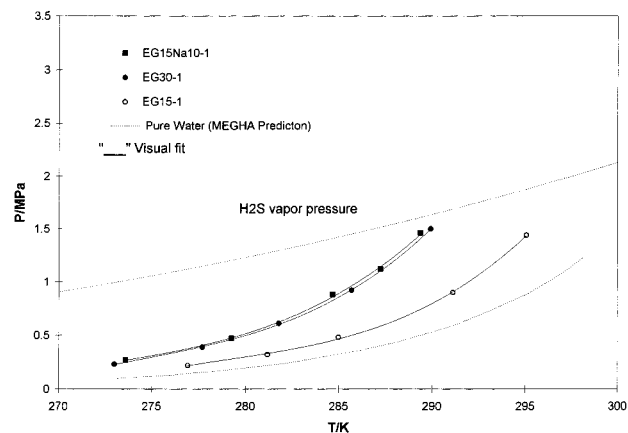


Figure 1. Experimental hydrate equilibrium conditions for hydrogen sulfide in aqueous solutions containing ethylene glycol and sodium chloride.

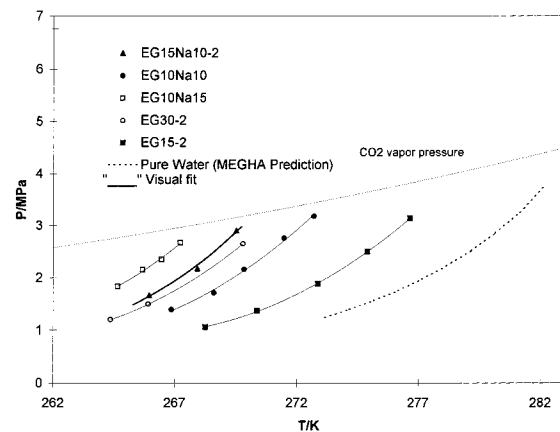


Figure 2. Experimental hydrate equilibrium conditions for carbon dioxide in aqueous solutions containing ethylene glycol and sodium chloride.

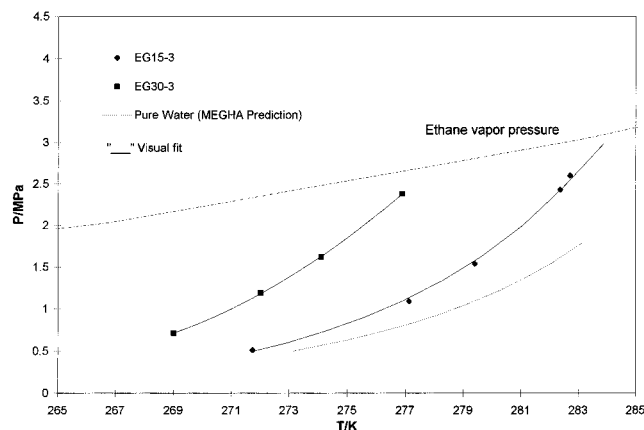


Figure 3. Experimental hydrate equilibrium conditions for ethane in aqueous solutions containing ethylene glycol.

Table 4. Experimental Hydrate Equilibrium Conditions for Ethane in Aqueous Solutions of Ethylene Glycol

solution ID	T/K	P/MPa
EG15-3	271.73	0.51
	277.13	1.09
	279.40	1.54
	282.38	2.43
	282.72	2.60
EG30-3	269.01	0.71
	272.01	1.19
	274.10	1.62
	276.88	2.38

dashed lines in the figures represent predictions made using the computer program MEGHA for pure water. The program uses the Trebble–Bishnoi equation of state (Trebble and Bishnoi, 1988) for the vapor and liquid phases and the van der Waals–Platteeuw model (van der Waals and Platteeuw, 1959) for the solid hydrate phase. The predictions for pure water are shown to help estimate the inhibiting effects of ethylene glycol and its mixtures with sodium chloride. It is seen from the figures that these additives have significant inhibiting effects on the hydrate formation conditions. In Figure 2, the data on EG15Na10-2 and EG10Na15 solutions for carbon dioxide indicate that the sodium chloride on mass basis has more inhibiting effect than the ethylene glycol.

Conclusions

A study was carried out to obtain much needed experimental data for the incipient equilibrium hydrate formation conditions for hydrogen sulfide, carbon dioxide, and ethane in the presence of aqueous solutions of ethylene glycol and sodium chloride. The data are obtained in the temperature range 264–290 K and the pressure range 0.23–3.18 MPa using a variable-volume sapphire cell. Sodium chloride is found to have more inhibiting effect on a mass basis than ethylene glycol.

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