J. Chem. Eng. Data **2001,** *46,* 927−929

Equilibrium Conditions Hydrate Dissociation for a Ternary Mixture of Methane, Ethane, and Propane in Aqueous Solutions of Ethylene Glycol and Electrolytes

Zhi-Gao Sun

Shanghai Jiao Tong University, P.O. Box A9902091, Shanghai 200030, People's Republic of China

Shuan-Shi Fan,* Lei Shi, Yan-Kun Guo, and Kai-Hua Guo

Laboratory of Gas Hydrate & High-Pressure Fluid, Guangzhou Institute of Energy Conversion,
The Chinese Academy of Sciences, Guangzhou 510070, People's Republic of China

Hydrate dissociation conditions for a mixture of methane, ethane, and propane in aqueous solutions of ethylene glycol and electrolytes (NaCl/$CaCl_2$) were experimentally studied in the pressure range of (0.78 to 8.1) MPa and the temperature range of (263.52 to 288.96) K. A new variable-volume sapphire cell was used for the measurements.

Introduction

Clathrate hydrates are crystalline inclusion compounds formed by hydrogen-bonded water molecules enclathrating small gas molecules. The conditions of hydrate formation is important to the oil and gas industry for designing and operating equipment and pipelines in order that hydrate formation is avoided. Inhibitors such as methanol, ethylene glycol, and electrolytes are used in industrial operations, and in the real production environment, salts (electrolytes) are present in the formation water. These aspects have been reviewed by Sloan (1998). Equilibrium data are reported for carbon dioxide + electrolytes + methanol by Dholabhai et al. (1996), synthetic natural gas mixture + electrolytes + methanol by Mei et al. (1998), and a ternary mixture of methane, propane, and carbon dioxide, and a natural gas mixture + electrolytes + methanol by Bishnoi and Dholabhai (1999). There are a few studies reported (Robinson and Ng, 1986; Song and Kobayashi, 1989; Majumdar et al., 2000) involve ethylene glycol.

In this work, we systematically measure the hydrate formation conditions of a mixture of methane, ethane, and propane in the presence of aqueous solutions containing electrolytes and ethylene glycol. The measurements are made in the pressure range of (0.78 to 8.1) MPa and the temperature range of (263.52 to 288.96) K.

Experimental Apparatus

A schematic diagram of the experimental apparatus used in this work is shown in Figure 1. The equilibrium cell is a "full view" sapphire variable-volume cell with a movable piston, the maximum effective volume being ≈100 cm^3, the minimum effective volume being 13.6 cm^3, and the maximum working pressure being 40 MPa. The sapphire cell is immersed in an air bath; the working temperature range is (253 to 393) K.

The cell contents are mixed by a stirrer and a circulating pump, the stirrer obtained by the rotation of a helix with four blades. It is driven by a dc motor located at the end of the piston and a magnetic coupling. The gas circulation is provided by a variable flow driven by a dc motor, and the maximum flow is 21.5 cm^3/h. The cell pressure is measured using a TF01 400A absolute pressure transducer (0 to 40) MPa (PT) of accuracy about ±0.06% of the scale (i.e., 24 kPa). The cell temperature is measured using platinum resistance thermometers with an accuracy of ±0.1 K. The cell volume is adjusted by a movable piston. The signals of pressure, temperature, and volume are acquired by a data acquisition system driven by a personal computer. The cell pressure, cell temperature, cell volume, air bath temperature, flow, and stirring velocity data from the acquisition system are saved at preset sampling intervals on a computer hard disk. The maximum working pressure of the sample cylinder is about 40 MPa, and the maximum volume is ≈150 cm^3.

A gas chromatograph (GC) (model HP6890) is used to analyze the vapor-phase compositions. A computer with a data acquisition card allowed the control of the chromatograph and the acquisition, storage, and integration of the results.

Experimental Procedure

The gas mixture was purchased from Kede Gas Industry Corp., which is mixed by research-grade pure gas. We analyzed the composition of the mixture using a HP 6890 gas chromatograph before the experiments were started. The composition of the mixture is 91.96 mol % methane, 5.13 mol % ethane, and 2.91 mol % propane. Solubility of gases and vaporization of ethylene glycol were neglected during the experiments. Electrolytes and ethylene glycol were research-grade chemicals supplied by Guangzhou Chemical Reagent Co. Appropriate quantities of ethylene glycol, salts, and distilled water were weighed on an electronic balance with a readability of ±0.1 mg. The compositions of the aqueous solutions for this study are shown in Table 1.

The equilibrium experimental data were obtained using the "pressure search" procedure (Bishnoi and Dholabhai,

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* To whom correspondence should be addressed. E-mail: fanss@ms.giec.ac.cn.

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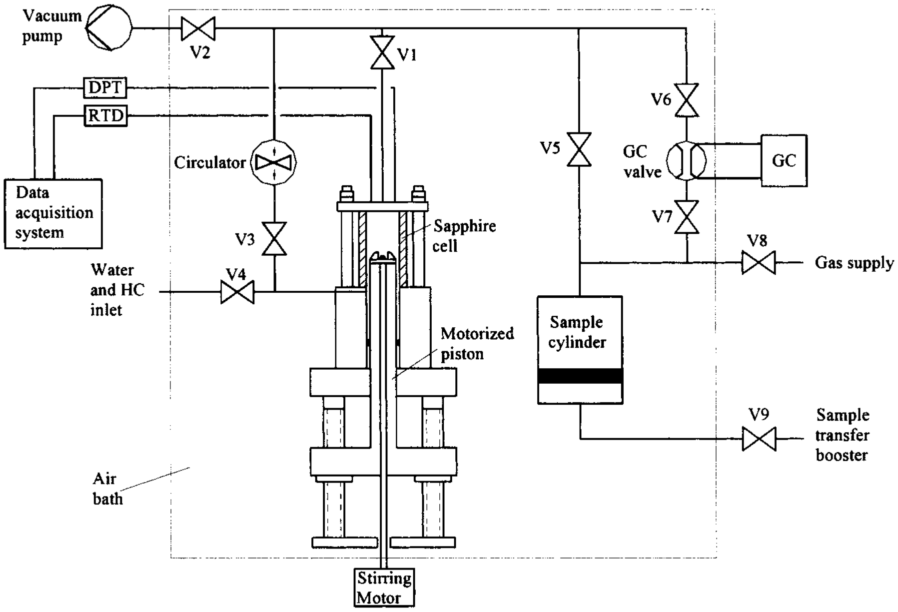

Figure 1. Schematic diagram of the experimental apparatus. DPT, differential pressure transducer; RTD, resistance temperature detector; V1−V9, valves.

Table 1. Composition of the Aqueous Solutions

aqueous solution	ethylene glycol[a] mass %	NaCl mass %	$CaCl_2$ mass %
EG10	10.06		
EG20	20.04		
EG30	29.99		
EG10Na10	9.96	9.94	
EG10Ca10	10.04		10.01
EG20Na10	20.00	9.99	
EG15Na5Ca5	15.03	4.99	5.01
EG20Na5Ca5	19.94	5.00	4.95

[a] All mass % values on a wet basis.

Table 2. Equilibrium Data on Gas Mixture Hydrate Formation in Aqueous Ethylene Glycol Solutions

solution	T K	P MPa	solution	T K	P MPa
pure water	288.96	5.37	pure water	277.91	1.43
	286.04	3.64		275.86	1.14
	282.05	2.29		273.58	0.91
	279.95	1.71			
EG10	284.97	4.54	EG10	276.40	1.57
	282.23	3.10		273.10	1.07
	279.09	2.09		270.19	0.78
EG20	283.15	5.13	EG20	273.10	1.57
	280.00	3.42		270.03	1.17
	276.16	2.29		267.11	0.91
EG30	279.18	5.17	EG30	270.09	2.00
	275.92	3.81		267.24	1.47
	273.41	2.91		264.76	1.12

Table 3. Equilibrium Data on Gas Mixture Hydrate Formation in Aqueous Ethylene Glycol and Electrolytes (NaCl, $CaCl_2$) Solutions

solution	T K	P MPa	solution	T K	P MPa
EG10Na10	281.97	5.67	EG10Na10	273.28	2.09
	279.20	4.25		270.96	1.57
	276.36	2.89		266.94	0.95
EG10Ca10	282.59	6.14	EG10Ca10	274.15	2.11
	279.16	3.91		270.89	1.43
	276.13	2.64		267.63	0.98
EG20Na10	279.04	6.92	EG20Na10	270.01	2.14
	276.16	4.65		266.97	1.47
	273.07	3.14		263.96	1.02
EG15Na5Ca5	280.27	6.44	EG15Na5Ca5	270.03	1.49
	278.41	4.64		267.92	1.24
	276.28	3.55		266.28	1.06
	272.86	2.18		264.62	0.89
EG20Na5Ca5	280.06	8.10	EG20Na5Ca5	269.67	1.69
	279.14	6.78		267.91	1.58
	276.39	4.51		266.44	1.26
	273.14	2.77		263.52	0.90

1993; Fan and Guo, 1999). The cell was rinsed with distilled water two times. Air was evacuated by the vacuum pump. Approximately 15 cm^3 of the aqueous solution was charged into the cell for each experiment. The presence of hydrates in the cell was determined visually in the equilibrium cell. Once the solution in the cell reached the desired temperature, the pressure of the cell was raised to a pressure exceeding the estimated equilibrium pressure by about 1.0 MPa. A large amount of hydrates were observed. The pressure then decreased by the cell piston being moved to decompose the hydrates. The procedure was repeated two times for each experimental run. The hydrates were formed and the equilibrium pressure was established using the pressure search method. The temperature and pressure are considered the equilibrium conditions when a small number of very tiny hydrate crystals in the cell remain stable for an extended period of time (3−4 h). The pressure in the cell was lowered by 0.05 MPa to confirm that all hydrates decomposed. A different temperature was subsequently selected, and the procedure was repeated to obtain the other hydrate equilibrium data.

Results and Discussion

Experimental equilibrium data for the gas mixture in the presence of different aqueous solutions of ethylene glycol, sodium chloride, and calcium chloride are tabulated in Tables 2 and 3. The data are also plotted in Figures 2 and 3. The solid lines shown in the figures are drawn by "visual fit" to clarify the trends of the experimental data.

Experiments were conducted with aqueous solutions of 10, 20, and 30 mass % ethylene glycol, and the results are also shown in Figure 2, which shows the inhibiting effects for each concentration of ethylene glycol.

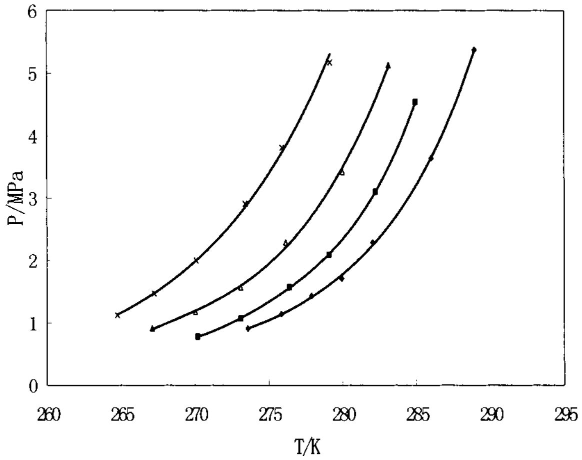

Figure 2. Experimental hydrate formation conditions for the gas mixture in aqueous solutions containing ethylene glycol: ◆, pure water; ■, EG10; △, EG20; ×, EG30; −, visual fit.

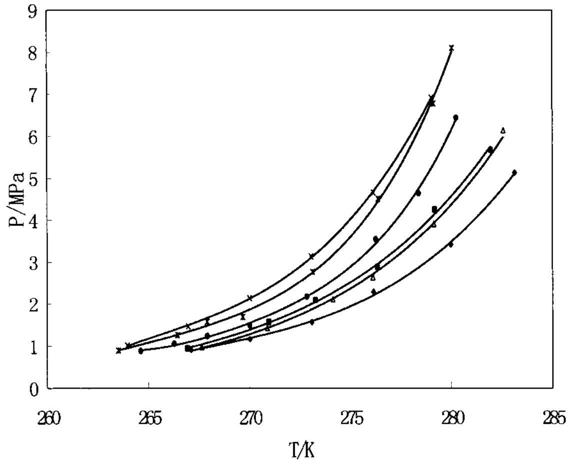

Figure 3. Experimental hydrate formation conditions for the gas mixture in aqueous solutions containing ethylene glycol and electrolyte (NaCl, $CaCl_2$): ◆, EG20; △, EG10Ca10; ■, EG10Na10; ●, EG15Na5Ca5; *, EG20Na5Ca5; ×, EG20Na10; −, visual fit.

The hydrate formation data in aqueous solutions of mixed ethylene glycol and electrolytes (NaCl, $CaCl_2$) are presented in Figure 3. The data on EG10Na10 (3.36 mol % ethylene glycol and 3.56 mol % sodium chloride) and EG10Ca10 (3.45 mol % ethylene glycol and 1.92 mol % calcium chloride) solutions for the gas mixture indicate that sodium chloride on a mass basis has a more inhibiting effect than calcium chloride. The experimental data on EG10Ca10 and EG20 (6.78 mol % ethylene glycol) show that ethylene glycol on a mass basis has a lower inhibiting effect than calcium chloride. Similar conclusions have been reached by Bishnoi and Dholabhai (1999) and Mei et al. (1998).

Conclusions

The effect of ethylene glycol and electrolytes (NaCl/$CaCl_2$) on the formation of the gas mixture of methane, ethane, and propane clathrate hydrates is studied. The data were obtained in the pressure range of (0.78 to 8.1) MPa and the temperature range of (263.52 to 288.96) K using a variable-volume sapphire cell. Calcium chloride is a stronger inhibitor than ethylene glycol but weaker than sodium chloride on a mass basis.

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Received for review November 30, 2000. Accepted April 18, 2001. The work was supported by the Chinese Academy of Sciences Dean Foundation, Guangdong Provincial Natural Science Foundation of China (No. 990039), and Major State Basic Research Program of China (G2000026306).

JE000365Z