Equilibrium Data for Methane, Ethane, and Propane Incipient Hydrate Formation in Aqueous Solutions of Ethylene Glycol and Diethylene Glycol

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Equilibrium experimental data for methane, ethane, and propane incipient hydrate formation in the presence of diethylene glycol and that for propane in the presence of ethylene glycol were obtained. Forty-six experiments were performed in the temperature and pressure ranges (264 to 283) K and (0.181 to 4.5) MPa, respectively, using the pressure search method. The experimental data were compared with predictions made using a hydrate equilibrium calculation method. The average deviation between the experimental data and calculated values was found to be 4.91%.

Introduction

Hydrates are known to occur in a variety of natural gas handling facilities and processing equipment, under suitable conditions of pressure and temperature. Prevention of hydrate formation requires a large amount of capital and results in considerable operating expenses. Hydrate inhibition using chemical inhibitors is the most widely used method in the industry. Measurement of the effect of such inhibitors on the equilibrium gas hydrate formation conditions is required for the cost-effective design and operation of a process. These data can also be used to verify the available methods for predicting the hydrate incipient pressure or temperature.

Although ethylene glycol and diethylene glycol have been used as hydrate inhibitors for a number of years, the data on hydrate formation in the presence of such inhibitors are scarce. This work investigates theoretically and experimentally the inhibition effects of these inhibitors on hydrate equilibria. The equilibrium hydrate conditions for methane, ethane, and propane in aqueous solutions of ethylene glycol and diethylene glycol are experimentally obtained in the temperature range (264 to 283) K and the pressure range(0.181 to 4.5) MPa.

In this work, a computational method presented by Englezos et al.[1] is used to predict the depression effect of inhibitors on the hydrate formation condition. The predictive method utilizes the statistical thermodynamic model of van der Waals and Platteeuw[2] for describing the solid hydrate phase. The Trebble−Bishnoi equation of state[3,4] is used for modeling the thermodynamic behavior of liquid and vapor phases. The method is used to predict the hydrate inhibition effects of ethylene glycol and diethylene glycol on methane, ethane, and propane gas hydrates. The predictions were found to have an average deviation of 4.91%.

Apparatus and Procedure

The experimental hydrate equilibrium data in this work are obtained using the experimental apparatus and procedures similar to those described by Dholabhai et al.[5] and Mahadev and Bishnoi.[6] The schematic of the apparatus is shown in Figure 1. The heart of the apparatus is a high-pressure variable-volume equilibrium cell.[7−8]

The schematic of the cell is shown in Figure 2. The cell consists of top and bottom flanges, which hold a sapphire tube and have ports for charging the solution, thermocouples for temperature measurements, and gas inlets for pressure measurements and vapor-phase sampling. A movable piston is used to change the volume of the cell. The piston is inserted in an opening in the top flange. The piston and its head are held down by means of a bolt and flange assembly similar to the one used for the sapphire tube. The piston is moved up and down by means of a manual gear assembly attached to the piston head. A stir bar is used to mix the cell contents. The bar is coupled with a rotating magnet mounted on the shaft of a dc motor located underneath the cell. A pressure gauge and a differential pressure transmitter (DP) are used to measure the pressure of the cell. 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 uncertainly of 0.25% of the span. The temperatures in the cell are measured with thermocouples calibrated against a standard probe in the range 262−290 K with the standard deviation of the least-squares fit of 0.1 K. The signals from the DP and thermocouples are acquired with a data acquisition system driven by a personal computer (PC). The pressure and temperature data, which are monitored by using the data acquisition system, are saved at preset sampling intervals on a computer storage disk. A software package (Crosstalk) is used to establish communication between the PC and the MINISAFE data acquisition system. The equilibrium cell is immersed into a constant-temperature bath. The set point of the temperature controller of the refrigerated bath can be changed in multiples of 0.1 K. A refrigerated 50% (by volume) solution of ethylene glycol in water is used as the circulating coolant.

The appropriate quantities of ethylene glycol and diethylene glycol were weighed on a top loading Mettler balance with a readability of 0.001 g and added to a known mass

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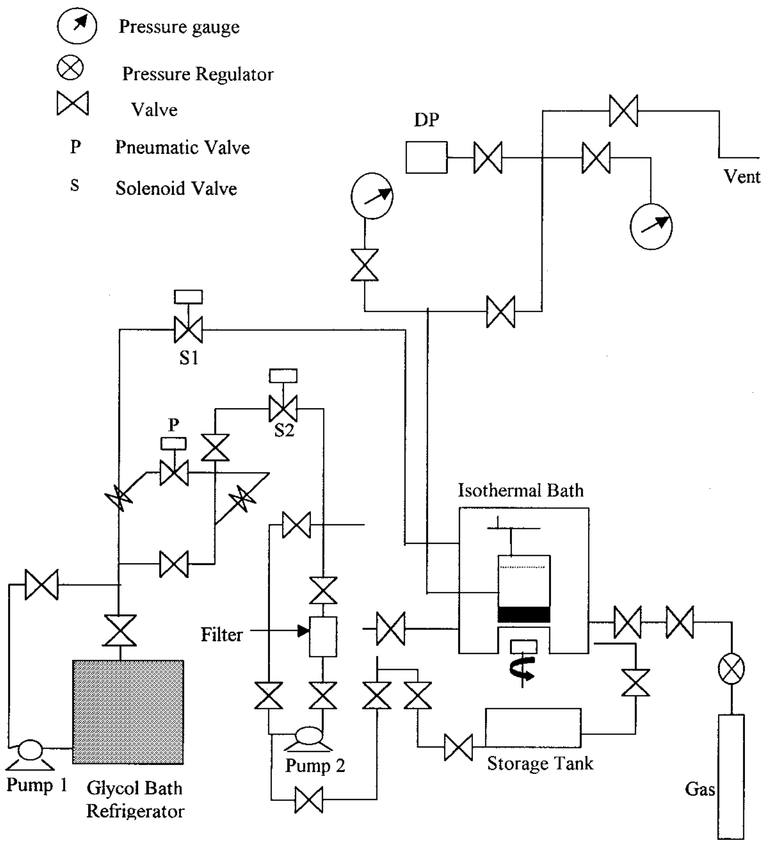

Figure 1. Schematic of the experimental apparatus.

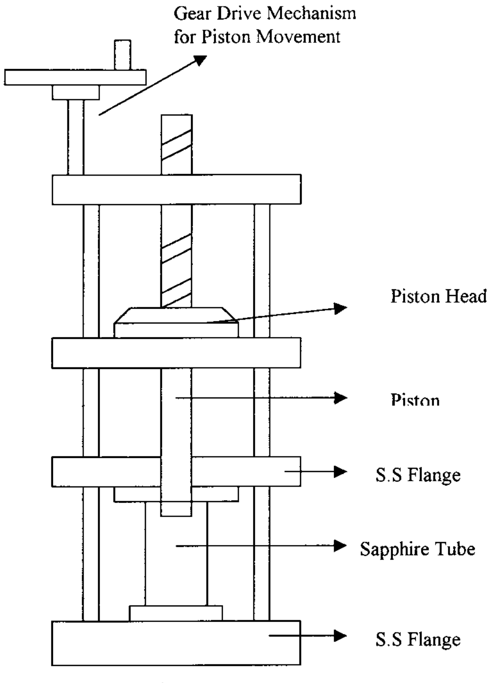

Figure 2. Schematic of the equilibrium cell.

Table 1. Experimental Hydrate Equilibrium Conditions for Propane in Aqueous Solutions of Ethylene Glycol[a]

solution i.d.	ethylene glycol mass %	T/K	P/kPa	T^1/K	P^1/kPa
Pro1_EG10	9.96	273.81	311.2	273.98	300.8
Pro2_EG10	9.96	274.48	412.8	274.78	378.8
Pro3_EG10	9.96	272.37	215	272.63	192.3
P1_EG15	14.99	271.42	210.1	271.42	199.4
P2_EG15	14.99	272.46	303	272.58	294.5
P3_EG15	14.99	273.79	426.7	273.78	395
P2_EG30	29.96	266.07	280.1	266.02	259.3
P3_EG30	29.96	265.23	240.7	265.35	196.9
P4_EG30	29.96	264.71	192	264.69	174.8
P5_EG30	29.96	266.39	304.4	266.58	281.6

[a] A superscript 1 denotes "no hydrate point"; that is, under these conditions all the hydrates decomposed.

Table 2. Experimental Hydrate Equilibrium Conditions for Methane in Aqueous Solutions of Diethylene Glycol

solution i.d.	diethylene glycol mass %	T/K	P/kPa	T^1/K	P^1/kPa
MET1DEG10	9.989	275.41	3457.4	275.52	3426.9
MET2DEG10	9.989	277.55	4445.2	277.67	4380.1
MET3DEG10	9.989	273.01	2623.9	273.11	2587.9
MET4DEG10	9.989	270.73	2033.5	270.84	1982.5
MET1DEG15	14.99	274.25	3592.7	274.24	3513.6
MET2DEG15	14.99	269.72	2171.9	269.82	2135.6
MET3DEG15	14.99	272.02	2819.5	272.04	2782.4
MET1DEG25	24.94	268.25	2453.2	268.24	2458
MET2DEG25	24.94	267.14	2046.5	267.11	2071.6
MET3DEG25	24.94	271.09	3154.2	271.14	3113

[a] A superscript 1 denotes "no hydrate point"; that is, under these conditions all the hydrates decomposed.

of water to make the experimental solution. The cell was first rinsed with distilled water and then with the experimental solution. Methane of Ultra High Purity grade with a certified purity of 99.97% and Chemically Pure ethane and Instrument grade propane with certified purities of 99% and 99.5%, respectively, supplied by PRAXAIR, were used to flush the cell repeatedly before performing the experiments. An amount of 15 mL of the prepared solution was charged into the cell. Generally, for each solution four experiments were performed. The presence of hydrate in the cell was detected visually, and an equilibrium point was located by using the pressure search method.[9] In this method, the temperature of the system was kept constant by using the temperature-controlled bath. Once the system

Table 3. Experimental Hydrate Equilibrium Conditions for Ethane in Aqueous Solutions of Diethylene Glycol[a]

solution i.d.	diethylene glycol mass %	T/K	P/kPa	T^1/K	P^1/kPa
ET1DEG10	9.98	275.37	703.7	275.5	663.3
ET2DEG10	9.98	277.86	956	277.91	912.9
ET3DEG10	9.98	279.32	1182.7	279.75	1161
ET4DEG10	9.98	280.72	1383.6	280.7	1360.3
ET5DEG10	9.98	272.38	1793.5	282.4	1763.6
ET1DEG15	14.97	279.77	1480.8	280.02	1375.6
ET2DEG15	14.97	274.83	679.5	274.73	654.7
ET3DEG15	14.97	277.43	1034.2	277.57	999
ET4DEG15	14.97	281.7	1661.5	281.49	1643.9
ET5DEG15	14.97	282.77	2069.9	282.74	2029.5
ET1DEG25	24.836	279.22	1650	279.25	1612.3
ET2DEG25	24.836	277.27	1251.6	277.22	1220.6
ET3DEG25	24.836	275.16	889.4	275.1	870.2
ET4DEG25	24.836	281.21	2292.9	281.26	2264.9

[a] A superscript 1 denotes "no hydrate point"; that is, under these conditions all the hydrates decomposed.

Table 4. Experimental Hydrate Equilibrium Conditions for Propane in Aqueous Solutions of Diethylene Glycol[a]

solution i.d.	diethylene glycol mass %	T/K	P/kPa	T^1/K	P^1/kPa
P1DEG10	9.97	273.94	236.1	273.94	231.1
P2DEG10	9.97	274.9	314.1	275.05	293.5
P3DEG10	9.97	275.54	387	275.77	363.7
P4DEG10	9.97	272.84	178.2	272.87	167
P1DEG15	14.984	273.99	304.1	274.22	273.3
P2DEG15	14.984	274.78	385.5	274.83	355.2
P3DEG15	14.984	275.17	397.7	275.05	377.7
P4DEG15	14.984	272.62	235.4	272.89	210.3
P5DEG15	14.984	271.77	180.9	271.91	161.1
P1DEG30	29.915	269.5	246.1	269.8	238.7
P2DEG30	29.915	268.78	198.4	269	178
P3DEG30	29.915	268.16	181.6	268.39	164.20

[a] A superscript 1 denotes "no hydrate point"; that is, under these conditions all the hydrates decomposed.

reached the desired temperature, the pressure was raised sufficiently above the estimated equilibrium pressure and the hydrates were allowed to form. The pressure was then lowered by moving the cell piston to a value slightly lower than the expected pressure to decompose the hydrates. The procedure was repeated once more. Then the hydrates were formed again and the equilibrium pressure was established. The steady pressure and temperature at which a small quantity of the hydrates remains stable for an extended period of time (3−4 h) were taken as the equilibrium conditions. The pressure of the system was lowered by 50 kPa to confirm that all the hydrates decomposed. The temperature of the system was changed, and the procedure was repeated to obtain other equilibrium data.

Results and Discussion

Experimental data on methane, ethane, and propane gases in aqueous solutions of ethylene glycol and diethylene glycol are given in Tables 1−4. The results are also presented graphically in Figures 3−7. The calculated hydrate formation pressures using the computational scheme of Englezos et al.[1] are also shown in the figures (solid lines). The interaction parameters, required in Trebble−Bishnoi equation of state,[3−4] and the procedures used in their determination are given by Mahmoodaghdam.[10] The dotted lines in Figures 4 and 7 show the error bounds for the data points. As can be seen from these figures, the calculated results are within the error bounds. Three phase equilibrium data conditions of ethane in various diethylene glycol solutions are shown in Figure 6. Since the experimental errors for this system are much smaller than the scale of the *Y*-axis, they are not shown in the figure. The experimental data for the methane + diethylene glycol system are plotted in Figure 5. The experimental errors for this system are also much smaller compared to the scale of the *Y*-axis; hence, they are also omitted from the figures. The experimental data for ethane in the presence of ethylene glycol, obtained previously in our laboratory,[11] are also predicted, and the results are shown in Figure 3.

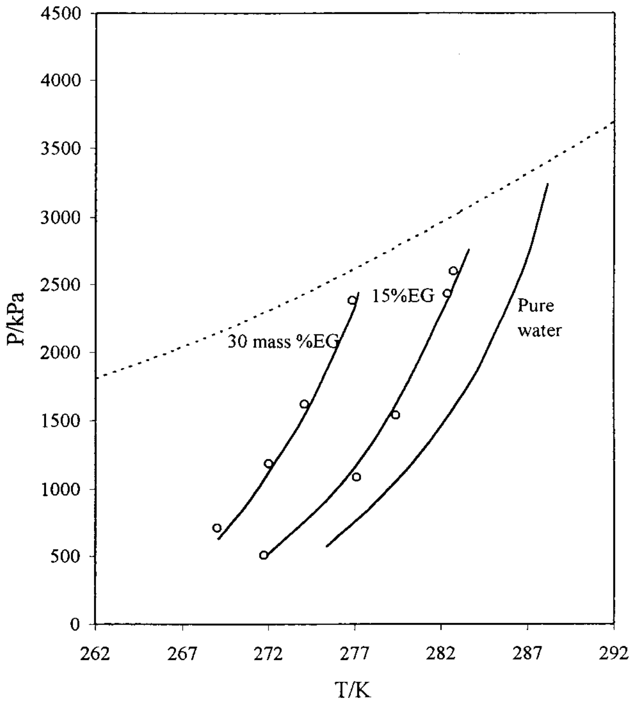

Figure 3. Experimental data and predicted ethane hydrate formation in aqueous solutions of ethylene glycol (EG): ○, experimental;[11] —, TB EOS prediction; - - -, ethane vapor pressure.

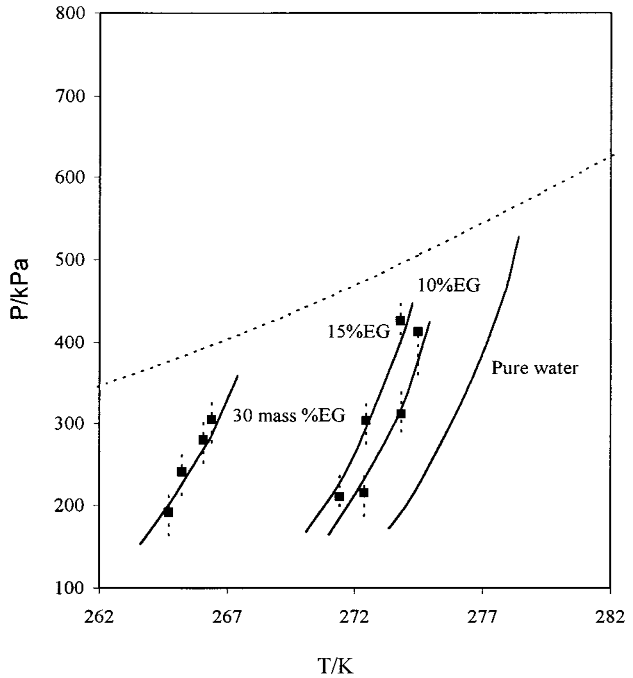

Figure 4. Experimental data and predicted propane hydrate formation in aqueous solutions of ethylene glycol (EG): ■, experimental (this work); —, TB EOS prediction; - - -, propane vapor pressure.

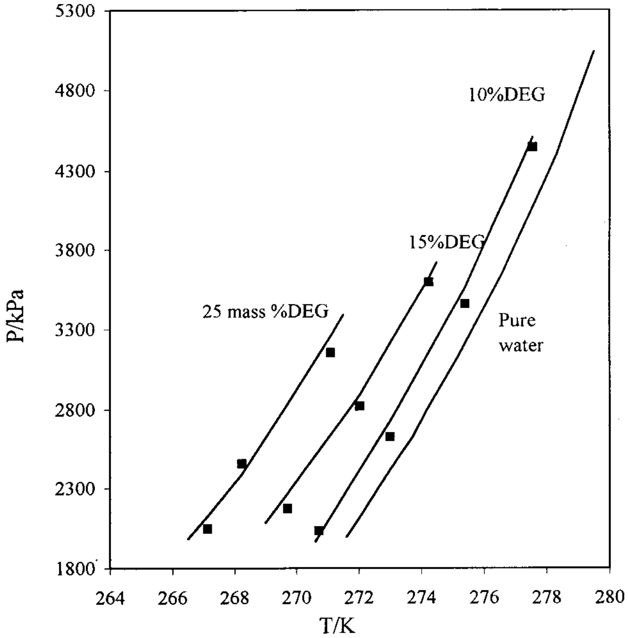

Figure 5. Experimental data and predicted methane hydrate formation in aqueous solutions of diethylene glycol (DEG): ■, experimental (this work); —, TB EOS prediction.

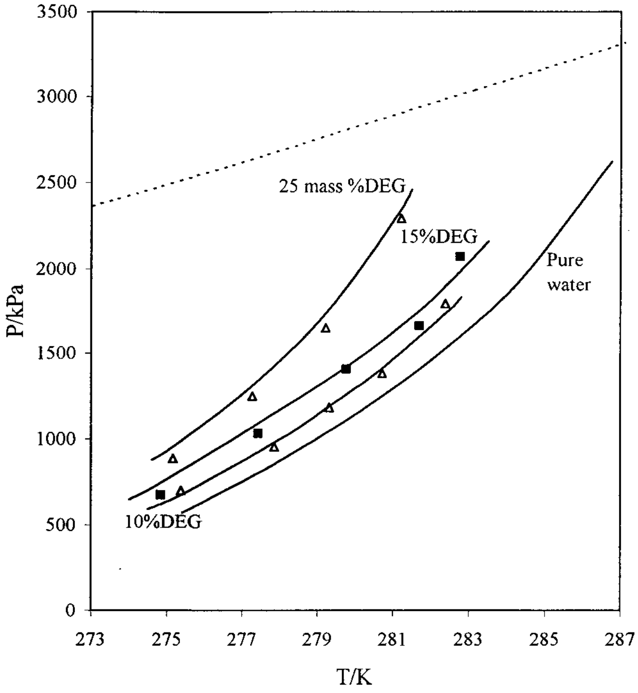

Figure 6. Experimental data and predicted ethane hydrate formation in aqueous solutions of diethylene glycol (DEG): △, experimental 10% and 25% DEG (this work); ■, experimental 15% DEG (this work); —, TB EOS prediction; - - -, ethane vapor pressure.

Conclusions

A study was carried out to measure the hydrate equilibrium formation data for methane, ethane, and propane gases in aqueous solutions of ethylene glycol and diethylene glycol. Forty-six experiments were performed in the temperature range (264 to 283) K and the pressure range (0.181 to 4.5) MPa. A predictive methodology is used to predict the incipient hydrate formation of the experimental data obtained in this work for methane, ethane, and propane in the presence of ethylene glycol and diethylene

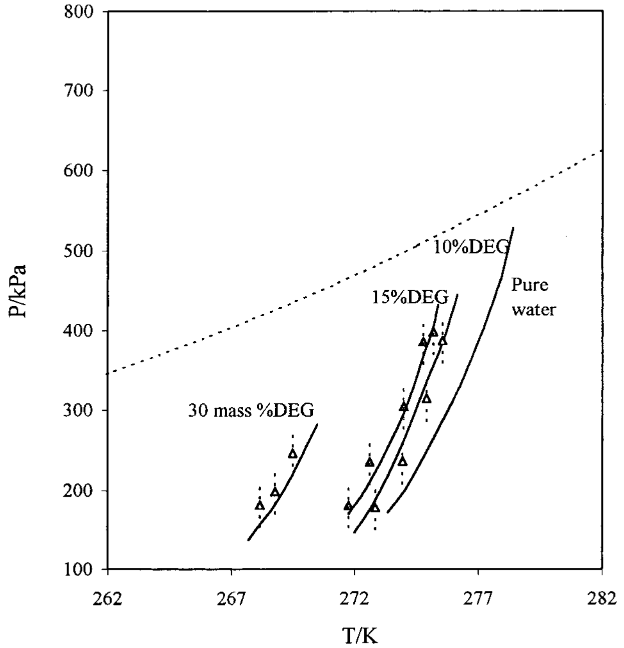

Figure 7. Experimental data and predicted propane hydrate formation in aqueous solutions of diethylene glycol (DEG): △, experimental (this work); —, TB EOS prediction; - - -, propane vapor pressure.

glycol. The predictions generally compared well with the experimental data.

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