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Experimental Measurements and Predictions of Dissociation Conditions for Carbon Dioxide and Methane Hydrates in the Presence of Triethylene Glycol Aqueous Solutions

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Experimental measurements and predictions for dissociation conditions of carbon dioxide hydrates in the presence of 0.05, 0.10, 0.15, and 0.20 mass fractions triethylene glycol aqueous solutions and methane hydrates in the presence of 0.245, 0.40, and 0.50 mass fractions triethylene glycol aqueous solutions are reported in this work. The data have been measured in temperature ranges of (264.7 to 282.6) K for carbon dioxide hydrates and (264.8 to 275.8) K for methane hydrates in the presence of triethylene glycol aqueous solutions. The experimental data have been measured using a reliable isochoric technique. A general correlation has been used for predicting hydrate dissociation conditions. Acceptable agreement has been achieved between experimental and predicted data with a maximum of 0.5 K deviations.

Introduction

Gas hydrates are a group of nonstoichiometric, icelike crystalline compounds formed through a combination of water and suitably sized "guest" molecules under low temperatures and high pressures. In the hydrate lattice, water molecules form hydrogen-bonded cagelike structures, encapsulating the guest molecules, which generally consist of low molecular diameter gases and organic compounds. A concise review of gas hydrates is given elsewhere.[1,2] Conditions of high fluid pressure and low temperature as well as presence of water leading to gas hydrate formation may be found in oil and gas production, transportation, and processing facilities. Formation of gas hydrates can lead to serious operational, economic, and safety problems in petroleum industry due to potential blockage of oil and gas equipment.[1] Organic inhibitors, such as alcohols and glycols, are normally used to inhibit gas hydrate formation. The presence of inhibitors normally reduces activity of water in aqueous phase, which shifts hydrate phase boundaries to high pressures/low temperatures.[1]

Reliable gas hydrate equilibrium data for natural gas main components in the presence/absence of inhibitors are necessary to develop and validate thermodynamic models for predicting hydrate phase boundaries of natural gases in the presence/absence of inhibitors. Many data have been reported for carbon dioxide and methane hydrates in the presence/absence of methanol and ethylene glycol aqueous solutions.[1] However, information for other organic inhibitors, such as triethylene glycol (TEG) are more limited. Ross and Toczylkin[3] presented experimental data on the effect of TEG on phase equilibrium of methane and ethane gas hydrates. Servio and Englezos[4] reported incipient equilibrium propane hydrate formation conditions in aqueous triethylene glycol solutions.

In this work, a reliable isochoric technique[5] has been used to perform experimental measurements of dissociation conditions for carbon dioxide and methane hydrates in the presence of triethylene glycol aqueous solutions. The data have been measured for dissociation conditions of carbon dioxide hydrates in the presence of 0.05, 0.10, 0.15, and 0.20 mass fractions triethylene glycol aqueous solutions in temperature ranges of (264.7 to 282.6) K and methane hydrates in the presence of 0.245, 0.40 and 0.50 mass fractions triethylene glycol aqueous solutions in temperature range of (264.8 to 275.8) K. A general correlation[6] has been used for predicting hydrate dissociation conditions and acceptable agreement has been achieved between experimental and predicted data with less than 0.5 K deviations.

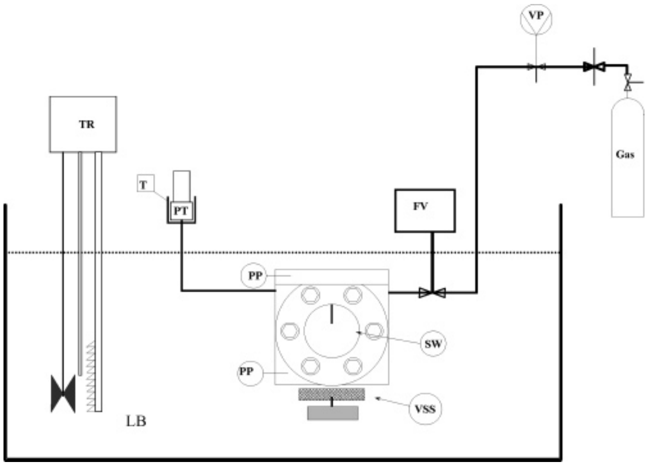

Figure 1. Schematic picture of the apparatus used for measuring hydrate dissociation points. FV, feeding valve; gas, carbon dioxide/methane; LB, liquid bath; PP, platinum probe; PT, pressure transducer; SW, sapphire window; T, temperature; TR, temperature regulator; VP, vacuum pump; VSS, variable speed stirring.

Experimental Section

Materials. Carbon dioxide and methane were purchased from Air Liquide and Messer Griesheim, respectively, with a certified purity higher than 0.9995 volume fraction. TEG was purchased from Aldrich with a certified purity >0.99 volume fraction and was carefully degassed before using. Distilled and deionized water was used after careful degassing.

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Table 1. Experimental Dissociation Data for Carbon Dioxide Hydrates in the Presence of TEG Aqueous Solutions (w_1 = Mass Percent of TEG in Aqueous Solution)

T/K	P/MPa	T/K	P/MPa	T/K	P/MPa	T/K	P/MPa
$w_1 = 5$ %		$w_1 = 10$ %		$w_1 = 15$ %		$w_1 = 20$ %	
273.7	1.41	274.9	1.78	273.5	1.60	264.7[a]	0.61
278.7	2.53	276.8	2.21	275.2	1.97	268.1[a]	0.91
280.5	3.15	278.3	2.63	277.1	2.45	274.3	1.90
282.6	4.23	280.4	3.45	279.1	3.11	277.4	2.78
				280.9	4.06		

[a] These data have not been shown in Figure 2.

Table 2. Experimental Dissociation Data for Methane Hydrates in the Presence of TEG Aqueous Solutions (w_1 = Mass Percent of TEG in Aqueous Solution)

T/K	P/MPa
$w_1 = 24.5$ %	
271.1	3.20
273.2	3.91
274.0	4.25
275.8	5.11
$w_1 = 40$ %	
266.1	3.07
268.6	3.95
270.1	4.61
271.2	5.05
$w_1 = 50$ %	
264.8	4.64
265.9	5.12

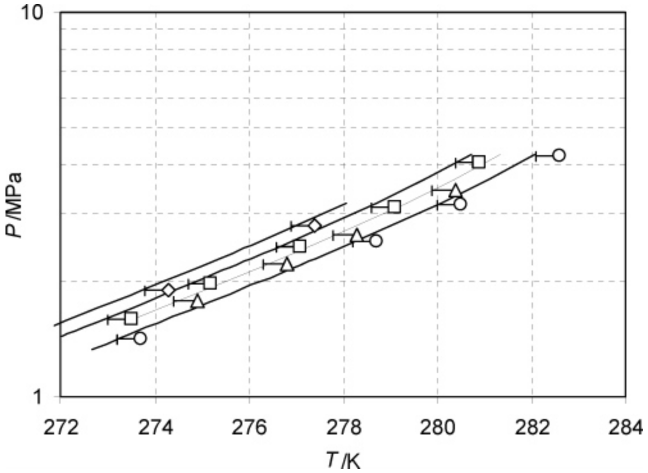

Figure 2. Experimental (this work) and predicted[6] dissociation conditions of carbon dioxide hydrates in the presence of different TEG aqueous solution (experimental data: ○, $w_1 = 5$ %; △, $w_1 = 10$ %; □, $w_1 = 15$ %; ◇, $w_1 = 20$ %). Error band: 0.5 K (w_1 = mass percent of TEG in aqueous solution).

Experimental Apparatus. The schematic picture of the apparatus used for generating data is presented in Figure 1. An equilibrium cell is immersed in a thermoregulated liquid bath with well stirred and suitable heating media; the temperature is controlled within 0.1 K. The cell has been constructed with 316 stainless steel. The cell contains two sapphire viewing windows in the front and rare end sides, which can be removed by opening their bolts. There is also an additional plate at the top. All the pieces of the cell are tightened by six bolts each and with O-rings of ethylene propylene to prevent any possible leakage. A motor driven mechanism is fixed just below the cell to stir cell contents with a magnetic stirrer inside to facilitate reaching fast equilibrium. For accurate temperature measurements in the cell and to check for thermal gradients, two platinum resistance thermometers (Pt100) are inserted inside thermowells drilled into the body of the equilibrium cell at two different levels and are connected to an HP data acquisition unit (HP34970A). These two Pt100 are carefully and periodically calibrated against a 25 Ω reference platinum resistance thermometer (TINSLEY Precision Instruments). The resulting uncertainty is not higher than 0.02 K. The 25 Ω reference platinum resistance thermometer was calibrated by the Laboratoire National d'Essais (Paris) on the basis of the 1990 International Temperature Scale (ITS 90). Pressures are measured by means of two pressure transducers (Druck, type PTX611): (0 to 0.6) for low pressures and vacuum and (0 to 8.0) MPa for high pressures connected to the HP data acquisition unit (HP34970A). The pressure transducers are maintained at constant temperature (temperature higher than the highest temperature of the study) by air-thermostat thermally controlled by a PID regulator (WEST instrument, model 6100). The pressure uncertainty is estimated to be within ±0.002 MPa, after a careful calibration against a dead weight balance (Desgranges & Huot 5202S, CP 0.3 to 40 MPa, Aubervilliers, France). The HP online data acquisition unit is connected to a desktop computer through a RS-232 interface. This complete data acquisition system allows real time measurements of temperature and pressure by correcting the observed values against calibration equations, which are recorded and presented graphically.

Experimental Method. The technique employed for measuring hydrate dissociation conditions is based on an isochoric pressure search method[5] at various temperatures when equilibrium is reached. The vessel containing the aqueous solution was immersed into the temperature-controlled bath, and the gas was supplied from a high-pressure cylinder through a pressure-regulating valve into the evacuated vessel. After temperature and pressure was stabilized, the valve in the line connecting the vessel and the cylinder was closed. Subsequently, temperature was decreased to form hydrate. Hydrate formation in the vessel was detected by a pressure drop. The temperature was then increased with steps of 0.1 K. At every temperature step, the temperature was kept constant for 4 h to achieve a steady equilibrium state in the vessel. In this way, a pressure−temperature diagram for each experimental run was obtained, from which hydrate dissociation point was determined. If the temperature is increased in the hydrate-forming region, hydrate crystals partially dissociate, thereby substantially increasing the pressure. If the temperature is increased outside the hydrate region, only a smaller increase in the pressure is observed as a result of the change in the phase equilibria of the fluids in the vessel. Consequently, the point at which the slope of pressure−temperature data plots changes sharply is considered to be the point at which all hydrate crystals dissociate and, hence, as the dissociation point.[1]

Hydrate dissociation pressure for methane hydrates in the presence of distilled water was initially measured at 278.2 K (i.e., 4.42 MPa) and was compared with the experimental measurement made by Thakore and Holder[7] (i.e., 4.50 MPa). The good agreement between the data shows the reliability of the experimental method used in this work.

Results and Discussions

Experimental dissociation points for carbon dioxide hydrates in the presence of 0.05, 0.10, 0.15, and 0.20 mass fractions TEG aqueous solutions and methane hydrates in the presence of 0.245, 0.40, and 0.50 mass fractions TEG aqueous solutions are reported in Tables 1 and 2 and are plotted in Figures 2 and 3, respectively. These figures also show predictions of a general correlation[6] for estimating hydrate inhibition effects of TEG aqueous solutions. Briefly, the following equation has been used for predicting hydrate dissociation temperature of a fluid

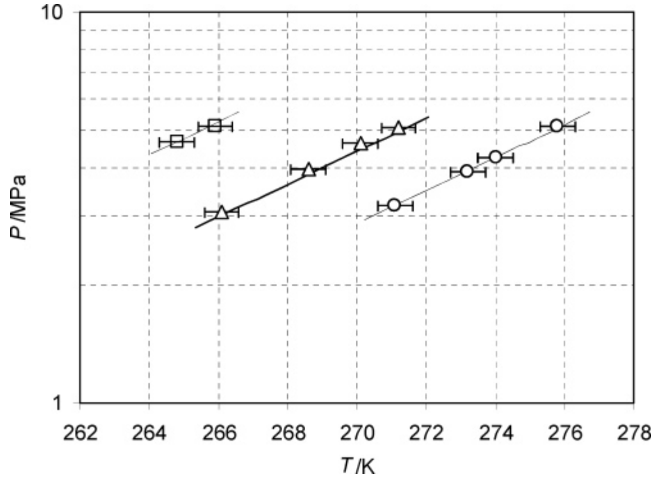

Figure 3. Experimental (this work) and predicted[6] dissociation conditions of methane hydrates in the presence of different TEG aqueous solutions (experimental data: ○, $w_1 = 24.5$ %; △, $w_1 = 40$ %; □, $w_1 = 50$ %). Error band: 0.5 K (w_1 = mass percent of TEG in aqueous solution).

in the presence of inhibitor (T in K) from hydrate suppression temperature (or suppression of hydrate dissociation temperature) (ΔT in K):

$$T = T_0 - \Delta T \qquad (1)$$

where T_0 (in K) stands for hydrate dissociation temperature of the same fluid system in the presence of distilled water. In the above equation, ΔT is calculated using the following equation:[6]

$$\Delta T = (C_1 w_1 + C_2 {w_1}^2 + C_3 {w_1}^3)(C_4 \ln(P) + C_5)(C_6(P_0 - 1000) + 1) \qquad (2)$$

where w_1, P, and P_0 are concentration of the inhibitor in liquid water phase (in mass percent), pressure of the system (in kPa), and dissociation pressure of fluid in the presence of distilled water at 273.15 K (in kPa). The constant C_i are given in the original manuscript for various inhibitors.[6]

In eq 1, T_0 can be calculated at any given pressure by using an appropriate predictive method such as the Heriot-Watt University hydrate (HWHYD) thermodynamic model,[8] which is capable of predicting different scenarios in hydrate phase equilibrium calculations. This model,[8] however, has not been developed for aqueous solutions containing high concentrations of TEG. A detailed description of this model is given elsewhere.[9,10] The model[8] is briefly based on equality of fugacity concept, which uses the Valderrama modification of the Patel−Teja equation of state[11] and nondensity dependent mixing rules[12] for modeling the fluid phases and the van der Waals and Platteeuw theory[13] for modeling the hydrate phase.

As can be seen in Figures 2 and 3, the agreements between the experimental and predicted data are generally acceptable. Experimental dissociation points for methane hydrates in the presence of TEG aqueous solutions show less than 0.5 K deviations. For CO_2 hydrates in the presence of TEG aqueous solutions, around 0.5 K deviations are observed, which can be attributed to the predictions of the general correlation,[6] as in this predictive method ΔT has been originally developed for hydrate suppression temperature of methane hydrates in the presence of inhibitor aqueous solution, which can also be used for sweet gases with low−intermediate concentrations of acid gases. However, the use of this ΔT for hydrate suppression temperature of acid gas hydrate due to the presence of inhibitor aqueous solution may be conservative.

Conclusions

New experimental dissociation data for carbon dioxide hydrates in the presence of 0.05, 0.10, 0.15, and 0.20 mass fractions triethylene glycol aqueous solutions in temperature range of (264.7 to 282.6) K and methane hydrates in the presence of 0.245, 0.40, and 0.50 mass fractions triethylene glycol aqueous solutions in temperature range of (264.8 to 275.8) K were reported in this work. The data, which were measured using a reliable isochoric technique, were compared with the predictions of a general correlation, and acceptable agreement between experimental and predicted data was achieved.

Note Added after ASAP Publication. This paper was published ASAP on July 11, 2007. Column headings in Table 1 were changed. The updated paper was reposted on August 6, 2007. Equation 2 was changed. The updated paper was reposted on August 14, 2007.

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