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Experimental Data and Predictions of Dissociation Conditions for Ethane and Propane Simple Hydrates in the Presence of Distilled Water and Methane, Ethane, Propane, and Carbon Dioxide Simple Hydrates in the Presence of Ethanol Aqueous Solutions

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Experimental gas hydrate dissociation data for ethane + distilled water, propane + distilled water, methane + 0.05 and 0.1 mass fraction ethanol aqueous solution, ethane + 0.05 and 0.1 mass fraction ethanol aqueous solution, propane + 0.05 and 0.1 mass fraction ethanol aqueous solution, and carbon dioxide + 0.05 and 0.1 mass fraction ethanol aqueous solution systems are reported herein. The new experimental data have been measured using an isochoric method. All the experimental data are compared with the predictions of a general correlation and a thermodynamic model. The agreements between the experimental and predicted data are generally found to be acceptable. The hydrate dissociation data for ethane + distilled water and propane + distilled water systems are also compared with some experimental data reported in the literature, and acceptable agreements between the data indicate the reliability of the experimental technique used in this study.

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 elevated pressures. In the gas hydrate lattice, water molecules form hydrogen-bonded cagelike structures, encapsulating the guest molecules, which generally consist of low molecular diameter gases and organic compounds.[1] Suitable conditions for gas hydrate formation commonly occur during hydrocarbon production and exploration operations.[1] Gas hydrate formation can cause flow restriction and blockage, which can lead to serious operational, economic, and safety problems. Thermodynamic inhibitors, such as alcohols and glycols, are normally used to inhibit gas hydrate formation.[1] The presence of inhibitors usually reduces the activity of water in the 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. Many data have been reported for gas hydrates of these components in the presence/absence of methanol and ethylene glycol aqueous solutions.[1] However, information for other organic inhibitors is limited.[1]

In this communication, we report experimental hydrate dissociation data for ethane and propane + distilled water and methane, ethane, propane, and carbon dioxide + ethanol aqueous solution systems, which have been measured based on our previous experimental work,[2] which takes advantage of an isochoric technique.[3] The hydrate dissociation data have been measured for ethane + distilled water in the (275.2 to 282.1) K temperature range, for propane + distilled water in the (274.6 to 278.3) K temperature range, for methane + 0.05 mass fraction ethanol aqueous solution in the (273.9 to 280.1) K temperature range, for methane + 0.1 mass fraction ethanol aqueous solution in the (271.1 to 280.2) K temperature range, for ethane + 0.05 mass fraction ethanol aqueous solution in the (273.6 to 280) K temperature range, for ethane + 0.1 mass fraction ethanol aqueous solution in the (274.4 to 282) K temperature range, for propane + 0.05 mass fraction ethanol aqueous solution in the (272.5 to 276.6) K temperature range, for propane + 0.1 mass fraction ethanol aqueous solution in the (272.0 to 275.0) K temperature range, for carbon dioxide + 0.05 mass fraction ethanol aqueous solution in the (272.4 to 280.1) K temperature range, and for carbon dioxide + 0.1 mass fraction ethanol aqueous solution in the (271.3 to 278.3) K temperature range. The experimental hydrate dissociation data measured in this work are compared with the predictions of a general correlation[4] and a thermodynamic model,[5] and acceptable agreements between the experimental and the predicted data are found. The new gas hydrate dissociation data for ethane and propane simple hydrates in the presence of distilled water are also compared with some selected experimental data from the literature,[6–8] and the acceptable agreements between the data indicate the reliability of the experimental technique used in this study.

Experimental Section

Purities and suppliers of materials are provided in Table 1. A detailed description of the experimental setup used in this study is given elsewhere.[2] Briefly, the main part of the apparatus was a cylindrical vessel with two sapphire windows, which can withstand pressures higher than 10 MPa. A stirrer was installed in the vessel to agitate fluids and hydrate crystals inside the vessel. The vessel is immersed inside a temperature-controlled bath to maintain the temperature inside the vessel at a prescribed level. Two platinum probes (Pt100) inserted into the vessel are used to measure temperature and to check for equality of

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Table 1. Purities and Suppliers of Materials[a]

chemical	supplier	purity
methane	Messer Griesheim	99.995
ethane	Messer Griesheim	99.995
propane	Messer Griesheim	99.995
carbon dioxide	Air–Liquide	99.995
ethanol	Fisher Scientific	99.99

[a] Deionized water was used in all experiments.

temperatures within temperature measurement uncertainties, which is estimated to be better than 0.1 K. This temperature uncertainty estimation comes from careful calibration against a 25 Ω reference platinum probe. The pressure in the vessel is measured with a DRUCK pressure transducer. Pressure measurement uncertainties are estimated to be better than 5 kPa. The hydrate equilibrium conditions are measured with the batch, isochoric procedure.[3] The vessel containing the aqueous solution is immersed into the temperature-controlled bath, and the gas is supplied from a high-pressure cylinder through a pressure-regulating valve into the partially evacuated vessel. After getting temperature and pressure stability, the valve in the line connecting the vessel and the cylinder is closed. Subsequently, the temperature is slowly decreased to form hydrate. Hydrate formation in the vessel is detected by a pressure drop. The temperature is then increased with steps of 0.1 K. At every temperature step, the temperature is kept constant for 4 h to achieve a steady equilibrium state in the vessel. In this way, a pressure−temperature diagram is obtained for each experimental run, from which we determined the hydrate dissociation point. If 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.[9] 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 is the dissociation point.

Results and Discussions

All experimental dissociation points measured in this work are reported in Table 2 and are plotted in Figures 1 to 4. A semilogarithmic scale has been used in these figures to show the data consistency, as a logarithm of hydrate dissociation pressure versus temperature has approximately linear behavior. The figures also show predictions of a general correlation[4] and a thermodynamic model[5] (the HWHYD thermodynamic model) for estimating hydrate inhibition effects of ethanol aqueous solutions. Briefly, the following equation has been used for predicting the hydrate dissociation temperature of a fluid in the presence of an inhibitor (T in K) from the 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[4]

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

Table 2. Experimental Hydrate Dissociation Data for Ethane and Propane Simple Hydrates in the Presence of Distilled Water and Methane, Ethane, Propane, and Carbon Dioxide Simple Hydrates in the Presence of Ethanol Aqueous Solutions (w_1 = Mass % of Ethanol in Aqueous Solution)

T/K[a]	P/MPa[b]
Ethane + Distilled Water	
275.2	0.60
279.6	1.01
282.1	1.40
Propane + Distilled Water	
274.6	0.22
277.1	0.40
278.3	0.50
Methane + Ethanol Aqueous Solution ($w_1 = 5$)	
273.9	3.45
275.6	4.02
277.8	5.03
280.1	6.20
Methane + Ethanol Aqueous Solution ($w_1 = 10$)	
271.1	2.98
273.8	4.01
276.5	5.03
280.2	7.42
Ethane + Ethanol Aqueous Solution ($w_1 = 5$)	
273.6	0.59
276.0	0.81
277.7	1.04
280.0	1.34
Ethane + Ethanol Aqueous Solution ($w_1 = 10$)	
274.4	0.81
277.2	1.15
279.8	1.72
282.0	2.23
Propane + Ethanol Aqueous Solution ($w_1 = 5$)	
272.5	0.20
274.2	0.30
275.1	0.35
276.6	0.51
Propane + Ethanol Aqueous Solution ($w_1 = 10$)	
272.0	0.25
273.4	0.36
274.5	0.44
275.0	0.50
Carbon Dioxide + Ethanol Aqueous Solution ($w_1 = 5$)	
272.4	1.31
274.6	1.71
276.5	2.12
278.7	2.83
280.1	3.41
Carbon Dioxide + Ethanol Aqueous Solution ($w_1 = 10$)	
271.3	1.39
274.7	2.10
277.0	2.79
278.3	3.37

[a] Uncertainty on temperatures through calibrated platinum probes is estimated to be better than 0.1 K. [b] Uncertainty on pressures through a calibrated pressure transducer is estimated to be better than 5 kPa.

where w_1, P, and P_0 are concentration of the inhibitor in the aqueous phase (in mass %), pressure of the system (in kPa), and dissociation pressure of fluid in the presence of distilled water at 273.15 K (in kPa). The constants C_i are given in the original manuscript for various inhibitors.[4] These constants for ethanol are:[4] $C_1 = 1.118$, $C_2 = -4.48 \cdot 10^{-3}$, $C_3 = 6.979 \cdot 10^{-4}$, $C_4 = 5.85 \cdot 10^{-3}$, $C_5 = 2.25 \cdot 10^{-1}$, $C_6 = 3.4 \cdot 10^{-5}$.

In eq 1, T_0 can be calculated at any given pressure by using an appropriate predictive method such as the HWHYD thermodynamic model,[5] which is capable of predicting different scenarios in hydrate phase equilibrium calculations. A detailed description of this model is given elsewhere.[10,11] The model[5] is briefly based on the equality of fugacity concept, which uses the Valderrama modification of the Patel−Teja equation of

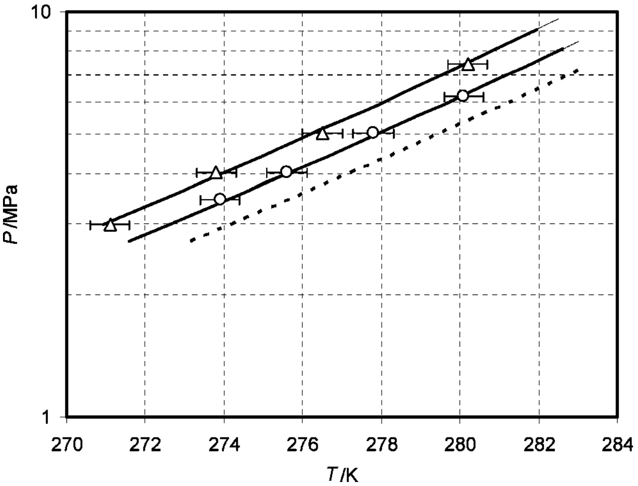

Figure 1. Experimental and predicted hydrate phase boundaries of methane. Points, experimental data: ○, methane + ethanol aqueous solution (w_1 = 5), this work; Δ, methane + ethanol aqueous solution (w_1 = 10), this work; bold solid lines, predictions of hydrate phase boundaries using general correlation[4] for the methane + ethanol aqueous solution systems; solid lines, predictions of hydrate phase boundaries using the thermodynamic model[5] for the methane + ethanol aqueous solution systems; dashed line, prediction of methane hydrate phase boundary in the presence of distilled water using the thermodynamic model[5] (w_1: mass % of ethanol in aqueous solution). Error band: 0.5 K.

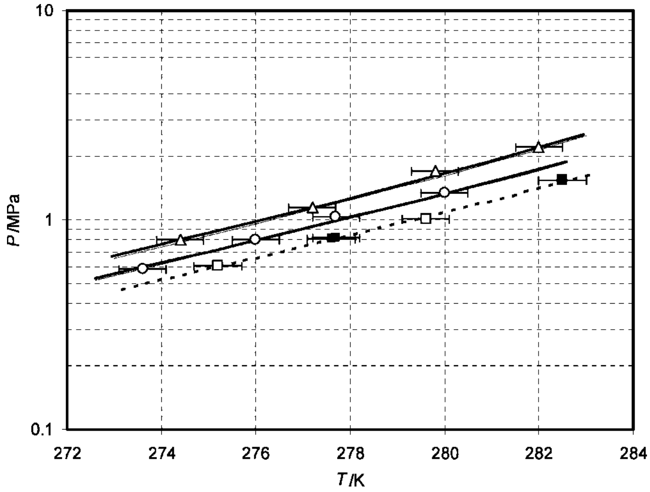

Figure 2. Experimental and predicted hydrate phase boundaries of ethane. Points, experimental data: ○, ethane + ethanol aqueous solution (w_1= 5), this work; Δ, ethane + ethanol aqueous solution (w_1= 10), this work; □, ethane + distilled water, this work; ■, ethane + distilled water, literature data;[6] bold solid lines, predictions of hydrate phase boundaries using general correlation[4] for the ethane + ethanol aqueous solution systems; solid lines, predictions of hydrate phase boundaries using the thermodynamic model[5] for the ethane + ethanol aqueous solution systems; dashed line, prediction of ethane hydrate phase boundary in the presence of distilled water using the thermodynamic model[5] (w_1: mass % of ethanol in aqueous solution). Error band: 0.5 K.

state[12] and nondensity dependent mixing rules[13] for modeling the fluid phases, and the van der Waals and Platteeuw theory[14] is used for modeling the hydrate phase.

As can be observed in the figures, the agreements between the experimental and predicted data are acceptable with less than 0.5 K deviations. Experimental dissociation points for ethane and propane simple hydrates have also been compared with some experimental data[6–8] reported in the literature. The acceptable agreements between experimental data for ethane and propane simple hydrates in the presence of distilled water demonstrate the reliability of the experimental technique used in this work.

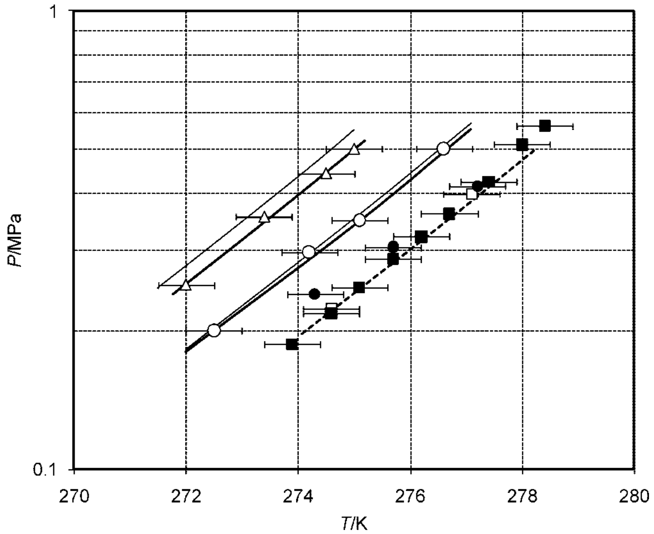

Figure 3. Experimental and predicted hydrate phase boundaries of propane. Points, experimental data: ○, propane + ethanol aqueous solution (w_1 = 5), this work; Δ, propane + ethanol aqueous solution (w_1 = 10), this work; □, propane + distilled water, this work; ■, propane + distilled water, literature data;[7] ●, propane + distilled water, literature data;[8] bold solid lines, predictions of hydrate phase boundary using general correlation[4] for the propane + ethanol aqueous solution systems; solid lines, predictions of hydrate phase boundary using the thermodynamic model[5] for the propane + ethanol aqueous solution systems; dashed line, prediction of propane hydrate phase boundary in the presence of distilled water using the thermodynamic model[5] (w_1: mass % of ethanol in aqueous solution). Error band: 0.5 K.

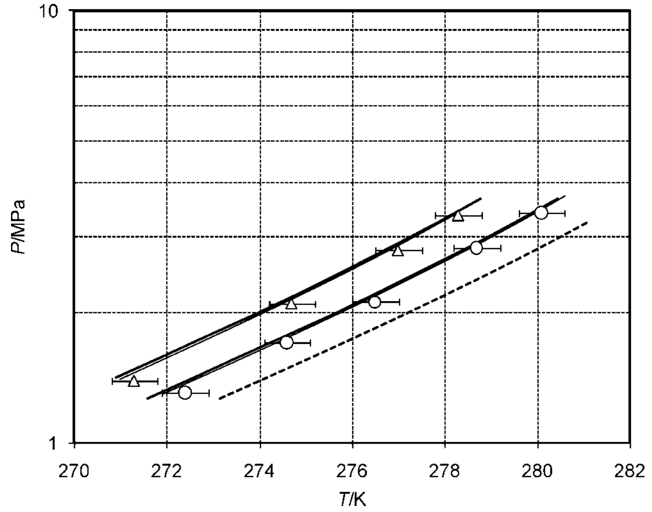

Figure 4. Experimental and predicted hydrate phase boundaries of carbon dioxide. Points, experimental data: ○, carbon dioxide + ethanol aqueous solution (w_1 = 5), this work; Δ, carbon dioxide + ethanol aqueous solution (w_1 = 10), this work; bold solid lines, predictions of hydrate phase boundary using general correlation[4] for the carbon dioxide + ethanol aqueous solution systems; solid lines, predictions of hydrate phase boundary using the thermodynamic model[5] for the carbon dioxide + ethanol aqueous solution systems; dashed line, prediction of carbon dioxide hydrate phase boundary in the presence of distilled water using the thermodynamic model[5] (w_1: mass % of ethanol in aqueous solution). Error band: 0.5 K.

Conclusions

Gas hydrate dissociation data for the systems of ethane + distilled water in the (275.2 to 282.1) K temperature range, propane + distilled water in the (274.6 to 278.3) K temperature range, methane + 0.05 mass fraction ethanol aqueous solution in the (273.9 to 280.1) K temperature range, methane + 0.1 mass fraction ethanol aqueous solution in the (271.1 to 280.2) K temperature range, ethane + 0.05 mass fraction ethanol aqueous solution in the (273.6 to 280) K temperature range, ethane + 0.1 mass fraction ethanol aqueous solution in the (274.4 to 282) K temperature range, propane + 0.05 mass fraction ethanol aqueous solution in the (272.5 to 276.6) K temperature range, propane + 0.1 mass fraction ethanol aqueous solution in the (272.0 to 275.0) K temperature range, carbon dioxide + 0.05 mass fraction ethanol aqueous solution in the (272.4 to 280.1) K temperature range, and carbon dioxide + 0.1 mass fraction ethanol aqueous solution in the (271.3 to 278.3) K temperature range were reported in this work. An isochoric method[2,3] was used for performing all the measurements. All the experimental data were compared with the predictions of a general correlation[4] and a thermodynamic model,[5] and acceptable agreements were found between experimental and predicted data. The experimental data for ethane + distilled water and propane + distilled water systems were also compared with some literature data, and the acceptable agreements between the data indicated the reliability of the experimental technique used in this work.

Note Added after ASAP Publication: This paper was published ASAP on November 14, 2007. Due to production error, Figures 1 and 2 were transposed. The revised paper was reposted on November 16, 2007.

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