Experimental Measurements and Predictions of Dissociation Conditions for Methane, Ethane, Propane, and Carbon Dioxide Simple Hydrates in the Presence of Diethylene Glycol Aqueous Solutions

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Experimental gas hydrate dissociation data for methane + 0.066 and 0.168 mass fractions diethylene glycol aqueous solution, ethane + 0.071 and 0.163 mass fractions diethylene glycol aqueous solution, propane + 0.073 and 0.164 mass fractions diethylene glycol aqueous solution, and carbon dioxide + 0.074 and 0.163 mass fractions diethylene glycol 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, and the agreements between the experimental and predicted data are found to be generally acceptable.

Introduction

Gas hydrates are solid crystalline compounds stabilized by the inclusion of suitably sized gas molecules inside cavities, of different sizes, formed by water molecules through hydrogen bonding. They resemble ice in appearance, but unlike ice, they may form at temperatures well above the ice point.[1] Suitable conditions for gas hydrate formation commonly occur during hydrocarbon production and exploration operations. Gas hydrate formation can block pipelines/transfer lines and lead to serious economic, operational, and safety problems.[1] Thermodynamic inhibitors, such as alcohols and glycols, are normally used to inhibit gas hydrate formation, which usually reduces the activity of water in the aqueous phase shifting hydrate phase boundaries to high pressures/low temperatures.[1] To develop and validate thermodynamic models and other predictive tools for predicting hydrate phase boundaries of natural gases, reliable gas hydrate equilibrium data for natural gas main components in the presence/absence of inhibitor aqueous solution are necessary.[1] Although many data have been reported for gas hydrates of these components in the presence/absence of methanol and ethylene glycol aqueous solutions, information for other organic inhibitors is limited.[1]

In this work, we report experimental hydrate dissociation data for methane, ethane, propane, and carbon dioxide single gases + diethylene glycol aqueous solution systems. The experimental method and apparatus are based on our previous experimental work, [2] which takes advantage of an isochoric technique.[3] The hydrate dissociation data have been measured for methane + 0.066 mass fraction diethylene glycol aqueous solution in the (278.5 to 282.5) K temperature range, methane + 0.168 mass fraction diethylene glycol aqueous solution in the (274.3 to 281.2) K temperature range, ethane + 0.071 mass fraction diethylene glycol aqueous solution in the (281.9 to 285.7) K temperature range, ethane + 0.163 mass fraction diethylene glycol aqueous solution in the (275.7 to 281.6) K temperature range, propane + 0.073 mass fraction diethylene glycol aqueous solution in the (273.7 to 277.0) K temperature range, propane + 0.164 mass fraction diethylene glycol aqueous solution in the (272.2 to 275.1) K temperature range, carbon dioxide + 0.074 mass fraction diethylene glycol aqueous solution in the (272.7 to 281.4) K temperature range, and carbon dioxide + 0.163 mass fraction diethylene glycol aqueous solution in the (272.1 to 279.8) 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[5–7] and acceptable agreements between the experimental and the predicted data are found.

Table 1. Purities and Suppliers of Materials[a]

chemical	supplier	purity/volume fraction
methane	Messer Griesheim	0.99995
ethane	Messer Griesheim	0.99995
propane	Messer Griesheim	0.99995
carbon dioxide	Air–Liquide	0.99995
diethylene glycol	Sigma-Aldrich	0.99

[a] Deionized water was used in all experiments.

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 is a cylindrical vessel with two sapphire windows, which can withstand pressures higher than 10 MPa. A stirrer inside the vessel allowed agitation of the fluids and hydrate crystals. The vessel was immersed inside a temperature-controlled bath to maintain its temperature at a prescribed level. Two platinum probes (Pt100) inserted into the vessel were used to measure temperature and check for equality of temperatures within temperature measurement uncertainties, which is estimated to be much less than 0.1 K. This temperature uncertainty estimation comes from careful calibration against a 25 Ω reference platinum probe (TINSLEY Precision Instruments). The pressure in the vessel was measured with a DRUCK pressure transducer. The pressure transducer was calibrated using a dead weight balance

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(Desgranges and Huot, model 520). Pressure measurement uncertainties are estimated to be less than 5 kPa. The hydrate equilibrium conditions were measured with the batch, isochoric procedure.[2,3] 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 air-free vessel. After getting temperature and pressure stability, the valve in the line connecting the vessel and the cylinder was closed. Subsequently, temperature was slowly 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 was 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.[8] 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.

Table 2. Experimental Gas Hydrate Dissociation Data for Methane, Ethane, Propane, and Carbon Dioxide + Diethylene Glycol Aqueous Solution Systems (w_1 = mass % of Diethylene Glycol in Aqueous Solution)

T/K[a]	P/MPa[b]
Methane + Diethylene Glycol Aqueous Solution ($w_1 = 6.6$)	
282.5	7.58
281.3	6.73
280.1	5.95
278.5	5.05
Methane + Diethylene Glycol Aqueous Solution ($w_1 = 16.8$)	
281.2	8.02
278.1	5.65
276.9	5.07
275.7	4.49
274.3	3.91
Ethane + Diethylene Glycol Aqueous Solution ($w_1 = 7.1$)	
285.7	2.80
285.0	2.55
283.3	2.02
281.9	1.61
Ethane + Diethylene Glycol Aqueous Solution ($w_1 = 16.3$)	
281.6	1.81
279.9	1.49
278.4	1.25
277.2	1.04
275.7	0.84
Propane + Diethylene Glycol Aqueous Solution ($w_1 = 7.3$)	
277.0	0.50
275.9	0.37
274.6	0.28
273.7	0.23
Propane + Diethylene Glycol Aqueous Solution ($w_1 = 16.4$)	
275.1	0.48
274.9	0.44
273.7	0.33
272.2	0.23
Carbon Dioxide + Diethylene Glycol Aqueous Solution ($w_1 = 7.4$)	
281.4	3.75
280.3	3.22
279.2	2.78
278.1	2.46
277.1	2.19
275.8	1.89
274.6	1.63
273.7	1.46
272.7	1.33
Carbon Dioxide + Diethylene Glycol Aqueous Solution ($w_1 = 16.3$)	
279.8	3.83
279.0	3.46
278.0	2.99
277.1	2.69
273.2	1.63
272.1	1.43

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

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 the 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[5–7] for estimating hydrate inhibition effects of diethylene glycol aqueous solutions. Briefly, the following equation has been used for predicting the hydrate dissociation temperature of a fluid in the presence of inhibitor (T in K) from the hydrate suppression temperature (or suppression of hydrate dissociation temperature) (ΔT in K)

$$T = T_0 - \Delta T \tag{1}$$

where T_0 (in K) stands for the 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]

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

where w_1, P, and P_0 are the concentration of the inhibitor in the aqueous phase (in mass %), the pressure of the system (in kPa), and the dissociation pressure of the 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 diethylene glycol are:[4] $C_1 = 0.343$, $C_2 = -3.47 \cdot 10^{-3}$, $C_3 = 2.044 \cdot 10^{-4}$, $C_4 = 1.8 \cdot 10^{-2}$, $C_5 = 3.346 \cdot 10^{-1}$, $C_6 = 2.74 \cdot 10^{-5}$.

In eq 1, T_0 can be calculated at any given pressure by using an appropriate predictive method such as the thermodynamic model[5–7] used in this work, which is capable of predicting different scenarios of hydrate phase equilibrium. A detailed description of this model is given elsewhere.[6,7] The model[5–7] is briefly based on the equality of fugacity concept, which uses the Valderrama modification of the Patel-Teja equation of state[9] and nondensity dependent mixing rules[10] for modeling the fluid phases, and the van der Waals and Platteeuw theory[11] 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.

Conclusions

Gas hydrate dissociation data for the systems of methane + 0.066 mass fraction diethylene glycol aqueous solution in the (278.5 to 282.5) K temperature range, methane + 0.168 mass

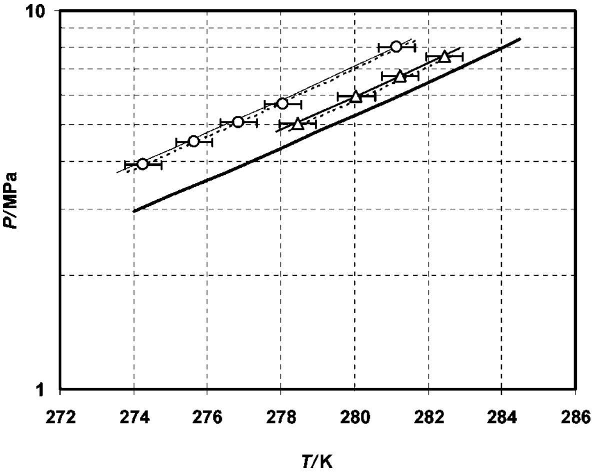

Figure 1. Experimental and predicted hydrate phase boundaries of methane. Symbols: experimental data. Δ, methane + diethylene glycol aqueous solution (w_1 = 6.6); ○, methane + diethylene glycol aqueous solution (w_1 = 16.8); solid lines, predictions of hydrate phase boundaries for the methane + diethylene glycol aqueous solution systems using the general correlation;[4] dashed lines, predictions of hydrate phase boundaries for the methane + diethylene glycol aqueous solution systems using the thermodynamic model;[5–7] bold solid line, prediction of hydrate phase boundary for the methane + distilled water system using the thermodynamic model[5–7] (w_1: mass % of diethylene glycol in aqueous solution). Error band: 0.5 K.

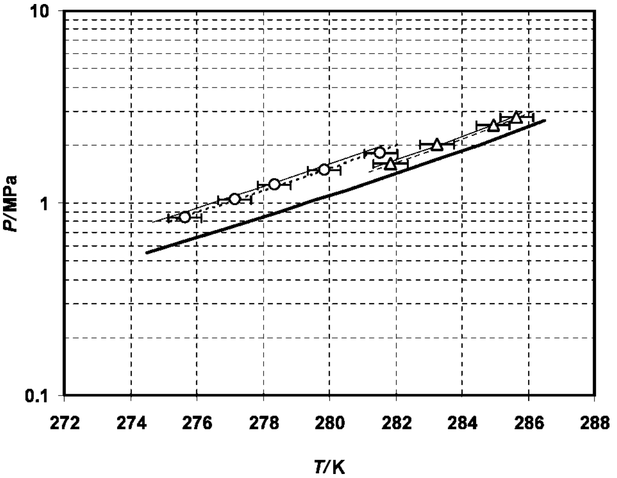

Figure 2. Experimental and predicted hydrate phase boundaries of ethane. Symbols: experimental data. Δ, ethane + diethylene glycol aqueous solution (w_1 = 7.1); ○, ethane + diethylene glycol aqueous solution (w_1 = 16.3); solid lines, predictions of hydrate phase boundarires for the ethane + diethylene glycol aqueous solution systems using the general correlation;[4] dashed lines, predictions of hydrate phase boundaries for the ethane + diethylene glycol aqueous solution systems using the thermodynamic model;[5–7] bold solid line, prediction of hydrate phase boundary for the ethane + distilled water system using the thermodynamic model[5–7] (w_1: mass % of diethylene glycol in aqueous solution). Error band: 0.5 K.

fraction diethylene glycol aqueous solution in the (274.3 to 281.2) K temperature range, ethane + 0.071 mass fraction diethylene glycol aqueous solution in the (281.9 to 285.7) K temperature range, ethane + 0.163 mass fraction diethylene glycol aqueous solution in the (275.7 to 281.6) K temperature range, propane + 0.073 mass fraction diethylene glycol aqueous solution in the (273.7 to 277.0) K temperature range, propane + 0.164 mass fraction diethylene glycol aqueous solution in the (272.2 to 275.1) K temperature range, carbon dioxide + 0.074 mass fraction diethylene glycol aqueous solution in the (272.7 to 281.4) K temperature range, and carbon dioxide + 0.163 mass fraction diethylene glycol aqueous solution in the (272.1 to 279.8) K temperature range were reported in this work.

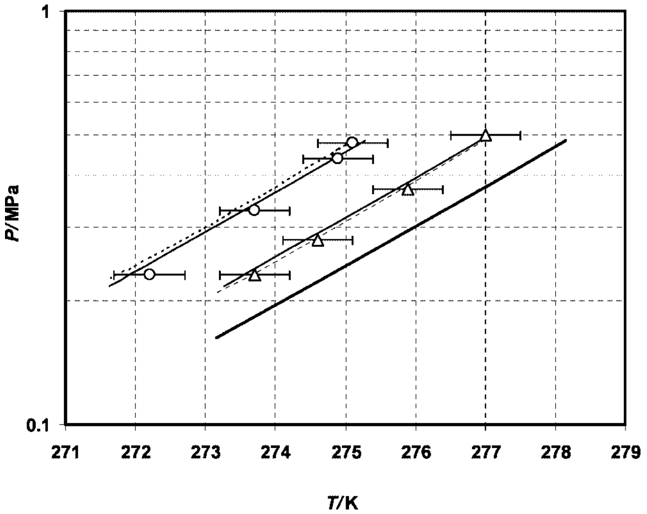

Figure 3. Experimental and predicted hydrate phase boundaries of propane. Symbols: experimental data. Δ, propane + diethylene glycol aqueous solution (w_1 = 7.3); ○, propane + diethylene glycol aqueous solution (w_1 = 16.4); solid lines, predictions of hydrate phase boundaries for the propane + diethylene glycol aqueous solution systems using the general correlation;[4] dashed lines, predictions of hydrate phase boundaries for the propane + diethylene glycol aqueous solutions systems using the thermodynamic model;[5–7] bold solid line, prediction of hydrate phase boundary for the propane + distilled water system using the thermodynamic model[5–7] (w_1: mass % of diethylene glycol in aqueous solution). Error band, 0.5 K.

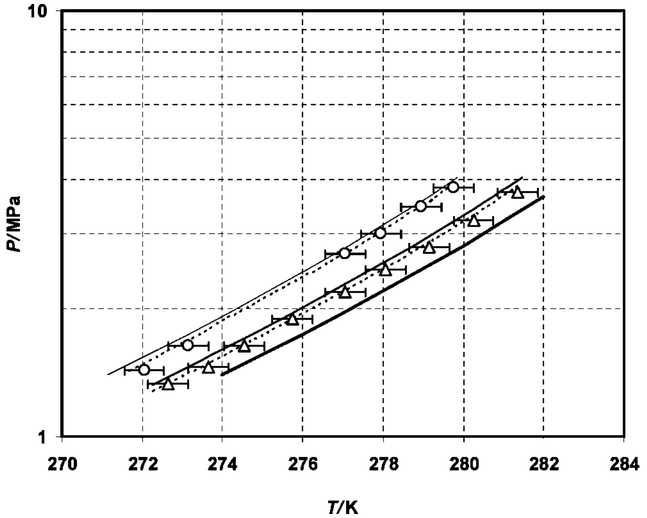

Figure 4. Experimental and predicted hydrate phase boundaries of carbon dioxide. Symbols: experimental data. Δ, carbon dioxide + diethylene glycol aqueous solution (w_1 = 7.4), ○, carbon dioxide + diethylene glycol aqueous solution (w_1 = 16.3); solid lines, predictions of hydrate phase boundaries for the carbon dioxide + diethylene glycol aqueous solution systems using the general correlation;[4] dashed lines, predictions of hydrate phase boundaries for the carbon dioxide + diethylene glycol aqueous solution systems using the thermodynamic model;[5–7] bold solid line, prediction of hydrate phase boundary for the carbon dioxide + distilled water system using the thermodynamic model[5–7] (w_1: mass % of diethylene glycol in aqueous solution). Error band: 0.5 K.

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,[5–7] and acceptable agreements were found between experimental and predicted data.

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