Experimental Data and Predictions of Dissociation Conditions for Ethane and Propane Simple Hydrates in the Presence of Methanol, Ethylene Glycol, and Triethylene Glycol Aqueous Solutions

Amir H. Mohammadi, Waheed Afzal, and Dominique Richon*

Mines Paris, ParisTech, CEP-TEP, CNRS FRE 2861, 35 Rue Saint Honoré, 77305 Fontainebleau, France

Experimental dissociation data for ethane and propane simple hydrates in the presence of (0.05 and 0.15) mass fractions of methanol, ethylene glycol, and triethylene glycol aqueous solutions are reported in this work. The experimental data have been measured using an isochoric method. All the experimental data are compared with the predictions of a general correlation (HWHYD correlation) and a thermodynamic model (HWHYD model). The agreements between the experimental and predicted data are generally found 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 and 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 the hydrate phase boundaries to high pressures and/or low temperatures.[1] To develop and validate thermodynamic models and other tools for predicting hydrate phase boundaries of natural gases, reliable gas hydrate equilibrium data for the main components of natural gases in the presence and absence of inhibitor aqueous solution are necessary.[1] Although many data have been reported for gas hydrates of methane and carbon dioxide in the presence and absence of methanol, ethylene glycol, and triethylene glycol aqueous solutions, information for gas hydrates of other components of natural gases in the presence of the above-mentioned aqueous solutions is limited.[1]

In this communication, we report experimental dissociation data for ethane and propane simple hydrates in the presence of (0.05 and 0.15) mass fractions of methanol, ethylene glycol, and triethylene glycol aqueous solutions. The data have been measured based on our previous experimental work,[2] which takes advantage of an isochoric method.[3] Table 1 summarizes the experiments carried out in terms of hydrate former, inhibitor, inhibitor concentration in the aqueous solution, and dissociation temperature ranges. The experimental hydrate dissociation data measured in this work are compared with the predictions of a general correlation (HWHYD correlation)[4] and a thermodynamic model (HWHYD model),[5] and acceptable agreements between the experimental and the predicted data are found.

Table 1. Dissociation Temperature Ranges Studied in this Work for Ethane and Propane Simple Hydrates in the Presence of Different Concentrations of Methanol, Ethylene Glycol, and Triethylene Glycol Aqueous Solutions

hydrate former	inhibitor	mass fraction of inhibitor in aqueous solution	hydrate dissociation temperature range/K
ethane	methanol	0.05	272.2 to 280.5
		0.15	268.2 to 278.9
	ethylene glycol	0.05	272.7 to 281.0
		0.15	269.7 to 279.6
	triethylene glycol	0.05	274.1 to 281.5
		0.15	274.0 to 281.1
propane	methanol	0.05	272.4 to 275.3
		0.15	266.3 to 269.9
	ethylene glycol	0.05	272.9 to 275.8
		0.15	269.8 to 273.7
	triethylene glycol	0.05	273.2 to 276.8
		0.15	273.7 and 275.0

Table 2. Purities and Suppliers of Materials[a]

chemical	supplier	purity (volume fraction)
ethane	Messer Griesheim	0.99995
propane	Messer Griesheim	0.99995
methanol	Aldrich	0.999
ethylene glycol	Aldrich	0.99
triethylene glycol	Aldrich	0.99

[a] Deionized water was used in all experiments.

Experimental Section

Purities and suppliers of materials are provided in Table 2. 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, which can withstand pressures higher than 10 MPa. The vessel has a volume of (57.5 ± 0.5) cm^3 with two sapphire windows. A magnetic stirrer ensures sufficient agitation to facilitate reaching equilibrium. The vessel was immersed inside a temperature-controlled bath to maintain the temperatures of study. 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 less than 0.1 K. This temperature uncertainty estimation comes from careful calibra-

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* Corresponding author. E-mail: richon@ensmp.fr. Tel.: +(33) 1 64 69 49 65. Fax: +(33) 1 64 69 49 68.

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Table 3. Experimental Dissociation Data for Ethane and Propane Simple Hydrates in the Presence of Methanol, Ethylene Glycol, and Triethylene Glycol Aqueous Solutions (w_1: Mass Fraction of Inhibitor in Aqueous Solution)

T/K[a]	P/MPa[b]
Ethane + Methanol Aqueous Solution ($w_1 = 0.05$)	
272.2	0.50
275.0	0.72
276.4	0.82
279.0	1.19
280.5	1.54
Ethane + Methanol Aqueous Solution ($w_1 = 0.15$)	
268.2	0.61
270.6	0.82
273.8	1.23
276.0	1.75
278.9	2.60
Propane + Methanol Aqueous Solution ($w_1 = 0.05$)	
272.4	0.21
273.6	0.28
274.8	0.35
275.3	0.41
Propane + Methanol Aqueous Solution ($w_1 = 0.15$)	
266.3	0.20
267.5	0.27
268.8	0.36
269.9	0.42
Ethane + Ethylene Glycol Aqueous Solution ($w_1 = 0.05$)	
272.7	0.49
274.1	0.61
276.3	0.79
278.8	1.10
281.0	1.45
Ethane + Ethylene Glycol Aqueous Solution ($w_1 = 0.15$)	
269.7	0.50
272.5	0.70
274.4	0.89
276.9	1.19
279.6	1.73
Propane + Ethylene Glycol Aqueous Solution ($w_1 = 0.05$)	
272.9	0.20
274.0	0.27
275.0	0.33
275.8	0.40
Propane + Ethylene Glycol Aqueous Solution ($w_1 = 0.15$)	
269.8	0.20
271.2	0.28
272.6	0.40
273.7	0.47
Ethane + Triethylene Glycol Aqueous Solution ($w_1 = 0.05$)	
274.1	0.58
275.3	0.69
277.5	0.90
279.3	1.10
281.5	1.45
Ethane + Triethylene Glycol Aqueous Solution ($w_1 = 0.15$)	
274.0	0.69
275.3	0.84
277.6	1.07
279.9	1.50
281.1	1.77
Propane + Triethylene Glycol Aqueous Solution ($w_1 = 0.05$)	
273.2	0.20
274.3	0.25
275.5	0.35
276.8	0.45
Propane + Triethylene Glycol Aqueous Solution ($w_1 = 0.15$)	
273.7	0.29
275.0	0.43

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

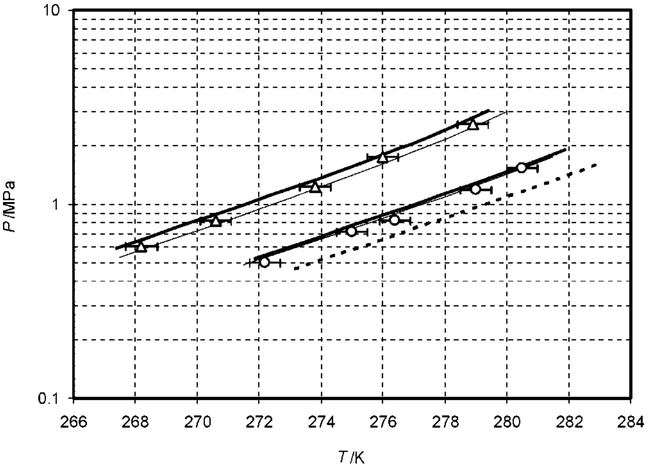

Figure 1. Experimental and predicted hydrate phase boundaries of ethane in the presence of methanol aqueous solutions. Symbols, experimental data: ○, ethane + methanol aqueous solution ($w_1 = 0.05$), this work; Δ, ethane + methanol aqueous solution ($w_1 = 0.15$), this work; bold solid lines, predictions of hydrate phase boundaries using general correlation[4] for the ethane + methanol aqueous solutions systems; solid lines, predictions of hydrate phase boundaries using the thermodynamic model[5] for the ethane + methanol 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 fraction of inhibitor in aqueous solution). Error band: 0.5 K.

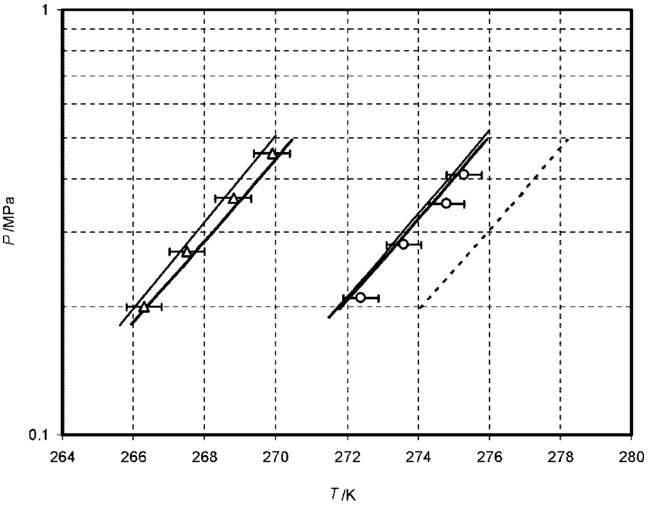

Figure 2. Experimental and predicted hydrate phase boundaries of propane in the presence of methanol aqueous solutions. Symbols, experimental data: ○, propane + methanol aqueous solution ($w_1 = 0.05$), this work; Δ, propane + methanol aqueous solution ($w_1 = 0.15$), this work; bold solid lines, predictions of hydrate phase boundaries using the general correlation[4] for the propane + methanol aqueous solutions systems; solid lines, predictions of hydrate phase boundaries using the thermodynamic model[5] for the propane + methanol 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 fraction of inhibitor in aqueous solution). Error band: 0.5 K.

tion against a 25 Ω reference platinum probe. The pressure in the vessel was measured with a DRUCK pressure transducer (Druck, type PTX611 for pressure ranges from (0 to 8) MPa). Pressure measurement accuracies are estimated to be better than 5 kPa. The hydrate dissociation points were measured with an isochoric pressure search procedure.[3] The vessel containing the aqueous solution (60 volume % of the vessel was filled by 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 partially evacuated

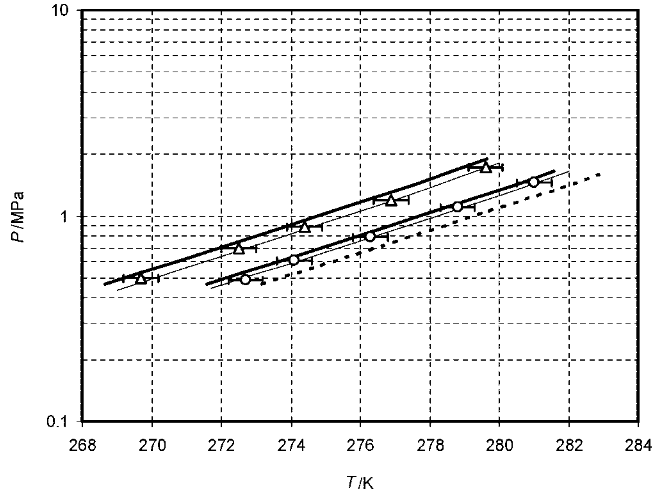

Figure 3. Experimental and predicted hydrate phase boundaries of ethane in the presence of ethylene glycol aqueous solutions. Symbols, experimental data: ○, ethane + ethylene glycol aqueous solution ($w_1 = 0.05$), this work; Δ, ethane + ethylene glycol aqueous solution ($w_1 = 0.15$), this work; bold solid lines, predictions of hydrate phase boundaries using the general correlation[4] for the ethane + ethylene glycol aqueous solution systems; solid lines, predictions of hydrate phase boundaries using the thermodynamic model[5] for the ethane + ethylene glycol aqueous solution systems; dashed line, Prediction of the ethane hydrate phase boundary in the presence of distilled water using the thermodynamic model[5] (w_1: mass fraction of inhibitor in aqueous solution). Error band: 0.5 K.

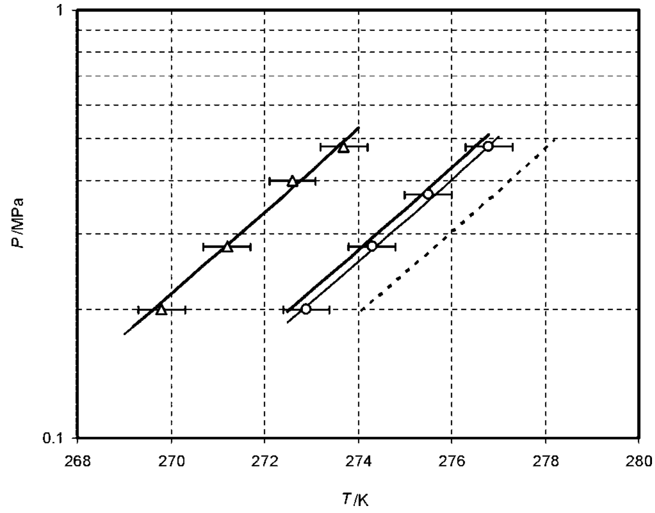

Figure 4. Experimental and predicted hydrate phase boundaries of propane in the presence of ethylene glycol aqueous solutions. Symbols, experimental data: ○, propane + ethylene glycol aqueous solution ($w_1 = 0.05$), this work; Δ, propane + ethylene glycol aqueous solution ($w_1 = 0.15$), this work; bold solid lines, predictions of hydrate phase boundaries using the general correlation[4] for the propane + ethylene glycol aqueous solution systems; solid lines, predictions of hydrate phase boundaries using the thermodynamic model[5] for the propane + ethylene glycol 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 fraction of inhibitor in aqueous solution). Error band: 0.5 K.

vessel. After getting temperature and pressure stability (far enough from the hydrate formation region), the valve between the vessel and the cylinder was closed. Subsequently, the temperature was slowly decreased to form the 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 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

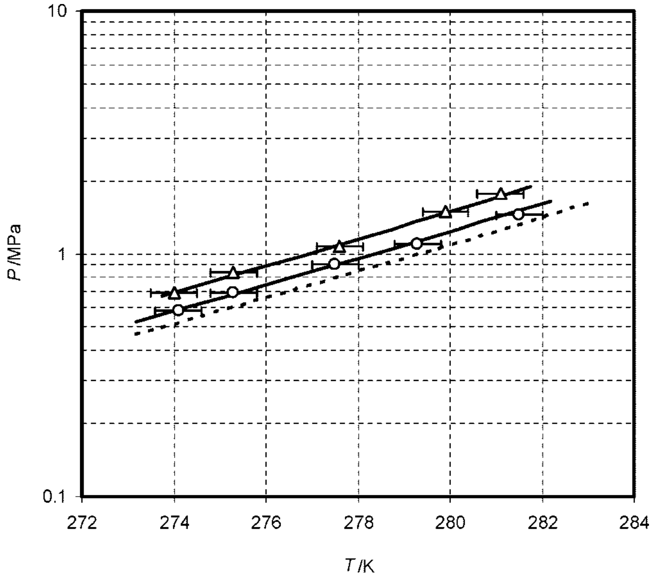

Figure 5. Experimental and predicted hydrate phase boundaries of ethane in the presence of triethylene glycol aqueous solutions. Symbols, experimental data: ○, ethane + triethylene glycol aqueous solution ($w_1 = 5$), this work; Δ, ethane + triethylene glycol aqueous solution ($w_1 = 15$), this work; bold solid lines, predictions of hydrate phase boundaries using the general correlation[4] for the ethane + triethylene glycol 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 fraction of inhibitor in aqueous solution). Error band: 0.5 K. The predictions of the thermodynamic model[5] have not been shown in this figure, as this model was not developed for triethylene glycol containing systems.

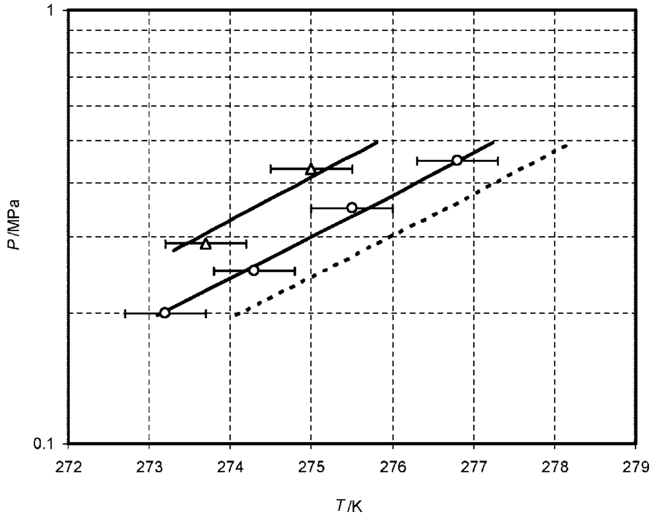

Figure 6. Experimental and predicted hydrate phase boundaries of propane in the presence of triethylene glycol aqueous solutions. Symbols, experimental data: ○, propane + triethylene glycol aqueous solution ($w_1 = 5$), this work; Δ, propane + triethylene glycol aqueous solution ($w_1 = 15$), this work; bold solid lines, predictions of hydrate phase boundaries using the general correlation[4] for the propane + triethylene glycol 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 fraction of inhibitor in aqueous solution). Error band: 0.5 K. The predictions of the thermodynamic model[5] have not been shown in this figure, as this model was not developed for triethylene glycol containing systems.

Table 4. Constants C_i in Equation 2 for Methanol, Ethylene Glycol, and Triethylene Glycol[4]

inhibitor	C_1	C_2	C_3	C_4	C_5	C_6
methanol	0.478	$7.17\cdot10^{-3}$	$-1.44\cdot10^{-5}$	$2.947\cdot10^{-2}$	$5.960\cdot10^{-1}$	$3.100\cdot10^{-5}$
ethylene glycol	38.93	$-5.22\cdot10^{-1}$	$1.767\cdot10^{-2}$	$3.503\cdot10^{-4}$	$5.083\cdot10^{-3}$	$2.650\cdot10^{-5}$
triethylene glycol	0.1964	$-5.81\cdot10^{-3}$	$1.393\cdot10^{-4}$	$2.855\cdot10^{-2}$	$8.540\cdot10^{-1}$	$3.240\cdot10^{-5}$

fluids in the vessel.[6] 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 have dissociated and hence as the dissociation point.

Results and Discussions

All experimental dissociation points measured in this work are reported in Table 3 and are plotted in Figures 1 to 6. 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 (HWHYD correlation)[4] and a thermodynamic model (HWHYD model)[5] for estimating hydrate inhibition effects of methanol, ethylene glycol, and triethylene glycol aqueous solutions. Briefly, the following equation has been used for predicting hydrate dissociation temperature, T, of a fluid in the presence of inhibitor from hydrate suppression temperature (or suppression of hydrate dissociation temperature, ΔT)

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

where T_0 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 (HWHYD correlation)[4]

$$\Delta T/\mathrm{K} = [C_1(w_1\cdot 100) + C_2(w_1\cdot 100)^2 + C_3(w_1\cdot 100)^3]\cdot[C_4\ln(P/\mathrm{kPa}) + C_5]\cdot[C_6((P_0 - 1000)/\mathrm{kPa}) + 1] \tag{2}$$

where w_1, P, and P_0 are the mass fraction of the inhibitor in the aqueous phase, the pressure of the system, and the dissociation pressure of fluid in the presence of pure water at 273.15 K. The constants C_i are given in the original manuscript for various inhibitors.[4] These constants for methanol, ethylene glycol, and triethylene glycol are reported in Table 4.[4] It should be mentioned that eq 2 has "six empirically determined constants" and should be used with care out of its application range.

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.[7,8] The model[5] is briefly based on the equality of fugacity in the various phases, 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] is used for modeling the hydrate phase. As can be observed in the figures, the agreements between the experimental and predicted data are generally acceptable with less than 0.5 K deviations. It should be noted that the predictions of the thermodynamic model[5] have not been shown in Figures 5 and 6 as this model was not developed for triethylene glycol containing systems.

Summary

Experimental dissociation data for ethane and propane simple hydrates in the presence of (0.05 and 0.15) mass fractions of methanol, ethylene glycol, and triethylene glycol aqueous solutions at various temperature ranges 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 (HWHYD correlation),[4] and a thermodynamic model (HWHYD model)[5] and acceptable agreements were found between experimental and predicted data.

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