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

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Experimental dissociation data for methane, ethane, and carbon dioxide simple hydrates in the presence of 0.1 and 0.4 mass fraction glycerol aqueous solutions and dissociation data for propane simple hydrates in the presence of 0.1 mass fraction glycerol aqueous solution are reported in this communication. The experimental data were generated using a reliable isochoric pressure-search method. The new experimental dissociation data for carbon dioxide simple hydrates in the presence of 0.1 mass fraction glycerol aqueous solution are compared with the experimental data reported in the literature and the agreements are generally found acceptable. All the experimental data are finally compared with the predictions of a general correlation and acceptable agreements between the experimental and predicted data are generally observed.

1. Introduction

One serious problem in hydrocarbon production, transportation, and processing is gas hydrate formation giving rise to equipment blockage, operational problems, and safety concerns.^{1–3} Gas hydrates are solid crystalline compounds physically resembling ice, in which small molecules (typically gases) are trapped inside cages of hydrogen bonded water molecules.^{1–3} To avoid formation of gas hydrates, organic inhibitors such as methanol and ethylene glycol are typically used.^{1–3} To develop and validate thermodynamic models for predicting hydrate phase boundaries of petroleum fluids, reliable gas hydrate equilibrium data for the main components of these fluids in the presence/absence of inhibitor aqueous solutions are therefore necessary.^{2,3} Although many experimental data have been reported for gas hydrates of these components in the presence of methanol and ethylene glycol aqueous solutions,¹ information for gas hydrates of petroleum fluids main components in the presence of other organic inhibitor aqueous solutions is limited.¹

In this communication, we report experimental dissociation data for methane, ethane, propane, and carbon dioxide simple hydrates in the presence of glycerol aqueous solutions, which have been measured based on our previous experimental work^{2,3} that takes advantage of a reliable isochoric pressure-search method.^{2–4} Table 1 summarizes the experiments carried out in terms of hydrate former, glycerol concentration in the aqueous solution, and dissociation temperature ranges. The experimental data on dissociation conditions of carbon dioxide simple hydrates in the presence of 0.1 mass fraction glycerol aqueous solution are successfully compared with the experimental data reported in the literature,⁵ which demonstrates the reliability of the experimental technique and the new experimental data reported in this work. The experimental hydrate dissociation

data are finally compared with the predictions of a general correlation,⁶ and acceptable agreements between the experimental and the predicted data are generally found.

2. Experimental Section

Purities and suppliers of materials are provided in Table 2. Figure 1 shows a schematic picture of the apparatus used for measuring hydrate dissociation points. A detailed description of the experimental setup used in this study is given elsewhere.^{2,3} Briefly, the main part of the apparatus is a cylindrical vessel, which can withstand pressures higher than 40 MPa. The vessel has a volume of $57.5 \pm 0.5 \text{ cm}^3$ 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

Table 1. Hydrate Dissociation Temperature (*T*) Ranges Studied in This Work for Methane, Ethane, Propane, and Carbon Dioxide Simple Hydrates in the Presence of Different Concentrations of Glycerol Aqueous Solutions (w_1 = Mass Fraction of Glycerol in Aqueous Solution)

hydrate former	w_1	<i>T</i> /K
methane	0.1	272.2–288.5
	0.4	266.1–279.0
ethane	0.1	272.4–286.5
	0.4	264.5–277.7
propane	0.1	272.7–276.8
carbon dioxide	0.1	271.5–279.7
	0.4	264.7–272.4

Table 2. Purities and Suppliers of Materials^a

chemical	supplier	purity
methane	Messer Griesheim	99.995 vol %
ethane	Messer Griesheim	99.995 vol %
propane	Messer Griesheim	99.95 vol %
carbon dioxide	Air Liquide	99.995 vol %
glycerol	Sigma	≥99.0 mol %

^a Deionized water was used in all experiments.

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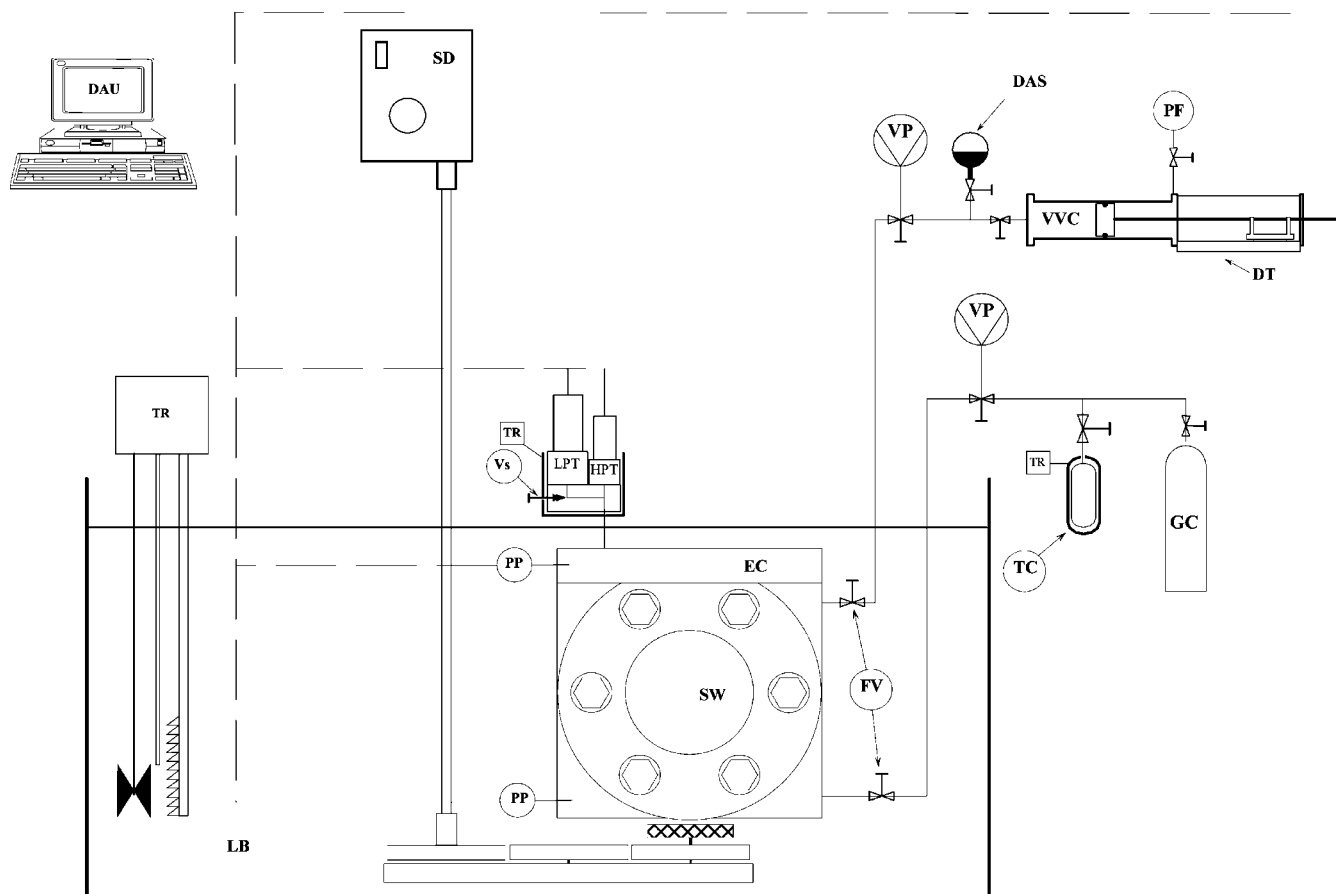


Figure 1. Schematic picture of the apparatus used for measuring hydrate dissociation conditions: DAS, degassed aqueous solution; DAU, data acquisition unit with central desktop computer; DT, displacement transducer; EC, equilibrium cell; FV, feeding valve; GC, gas cylinder; HPT, high pressure transducer (in use); LB, liquid bath for controlled cooling and heating cycles; LPT, low pressure transducer (out of service); PF, pressurizing fluid; PP, platinum resistance thermometer (platinum probe) for temperature; SD, stirring device coupled magnetically with the equilibrium cell; SW, sapphire window; TC, temperature controller; TR, temperature regulator; VP, vacuum pump; Vs, separating valve of LPT; VVC, variable volume cell.

platinum resistance thermometers (Pt100) inserted into the vessel were used to measure temperature and check for equality of temperatures within temperature measurement uncertainties, which are estimated to be less than 0.1 K. This temperature uncertainty estimation comes from careful calibration against a 25 Ω reference platinum resistance thermometer. The pressure in the vessel was measured with a DRUCK pressure transducer (Druck, type PTX611 for pressures up to 20 MPa). Pressure measurement accuracies are estimated to be better than 5 kPa. The hydrate dissociation points were measured with isochoric pressure-search procedure.^{2–4} The vessel containing the aqueous solution (50% by 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 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 pressure drop. The temperature was then increased with steps of 0.1 K. At every temperature step, the temperature was kept constant with sufficient time 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 (Figure 2). 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

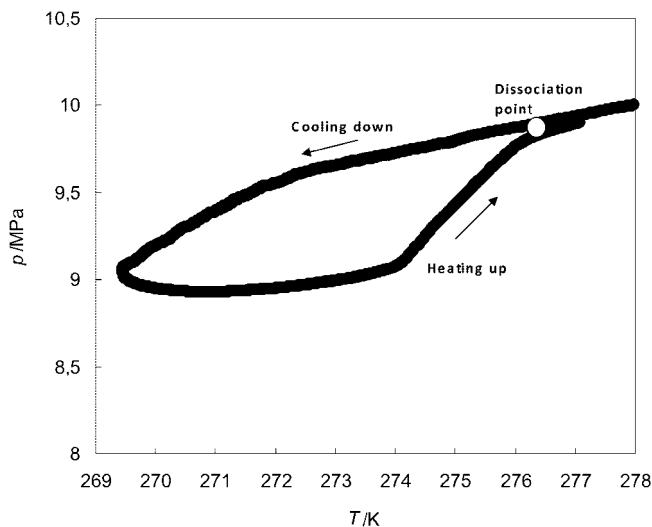


Figure 2. Pressure–temperature diagram for estimating dissociation point of methane hydrates in the presence of 0.4 mass fraction glycerol aqueous solution.

observed as a result of the change in the phase equilibria of the fluids in the vessel (see Figure 2).⁷ 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 is hence reported as the dissociation point.

Table 3. Experimental Dissociation Data for Methane, Ethane, Propane, and Carbon Dioxide Simple Hydrates in the Presence of Glycerol Aqueous Solutions (w_1 = Mass Fraction of Glycerol in Aqueous Solution)

T/K^a	p/MPa^b
methane + 0.1 mass fraction glycerol aqueous solution	
288.5	14.80
285.6	11.08
283.1	8.48
279.9	6.09
276.8	4.27
273.7	3.33
272.2	2.72
ethane + 0.1 mass fraction glycerol aqueous solution	
286.5	3.60
283.4	2.20
281.0	1.54
278.5	1.11
277.0	0.92
274.3	0.66
272.4	0.52
propane + 0.1 mass fraction glycerol aqueous solution	
276.8	0.52
275.7	0.44
274.6	0.35
272.7	0.24
carbon dioxide + 0.1 mass fraction glycerol aqueous solution	
279.7	3.39
278.2	2.75
276.8	2.32
275.2	1.92
273.5	1.56
271.5	1.25
methane + 0.4 mass fraction glycerol aqueous solution	
279.0	13.33
276.6	9.91
274.3	7.52
270.8	5.46
269.4	4.70
267.9	4.10
266.1	3.29
ethane + 0.4 mass fraction glycerol aqueous solution	
277.7	2.62
275.8	2.02
274.2	1.64
272.7	1.35
270.4	1.01
267.0	0.65
264.5	0.47
carbon dioxide + 0.4 mass fraction glycerol aqueous solution	
272.4	3.30
271.2	2.80
269.6	2.35
268.4	2.06
267.1	1.78
265.8	1.57
264.7	1.42

^a Uncertainty on temperatures through calibrated platinum resistance thermometers 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.

3. Results and Discussion

All dissociation data measured in this work are reported in Table 3 and are plotted in Figures 3 and 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 experimental data on dissociation conditions of carbon dioxide simple

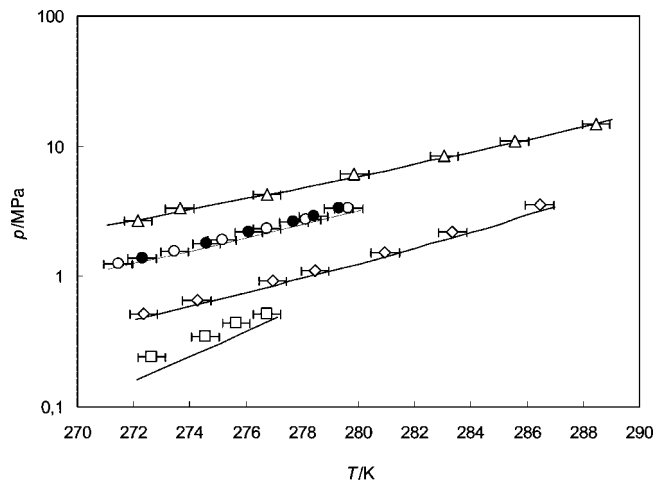


Figure 3. Experimental and predicted dissociation conditions of methane, ethane, propane, and carbon dioxide simple hydrates in the presence of 0.1 mass fraction glycerol aqueous solution. Symbols are for experimental dissociation conditions: Δ methane simple hydrates, this work; \circ carbon dioxide simple hydrates, this work; \bullet carbon dioxide simple hydrates, literature data;⁵ \diamond ethane simple hydrates, this work; \square propane simple hydrates, this work. The solid lines are predictions of hydrate dissociation conditions using general correlation.⁶ The error band is 0.5 K.

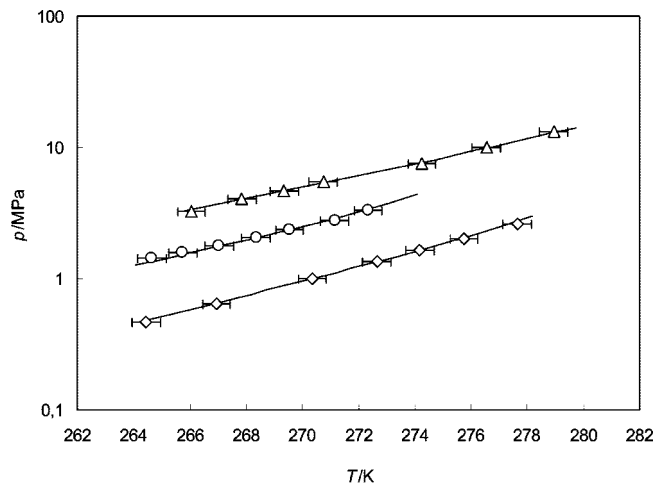


Figure 4. Experimental and predicted dissociation conditions of methane, ethane, and carbon dioxide simple hydrates in the presence of 0.4 mass fraction glycerol aqueous solution. Symbols are for experimental dissociation conditions: Δ methane simple hydrates, this work; \circ carbon dioxide simple hydrates, this work; \diamond ethane simple hydrates, this work. The solid lines are predictions of hydrate dissociation conditions using general correlation.⁶ The error band is 0.5 K.

hydrates in the presence of 0.1 mass fraction glycerol aqueous solution are compared with the experimental data reported in the literature.⁵ The acceptable agreement between the experimental data measured in this work and the experimental data reported in the literature⁵ demonstrates the reliability of the experimental technique and new data reported in this work. Figures 3 and 4 also show predictions of a general correlation⁶ for hydrate dissociation conditions. Briefly, the following equation has been used for predicting hydrate dissociation temperature of a fluid in the presence of inhibitor, T , from hydrate suppression temperature (or suppression of hydrate dissociation temperature) (ΔT):

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

where T_0 stands for hydrate dissociation temperature of the same fluid system in the presence of distilled water. In the above

Table 4. Constants c_i in Equation 2 for Glycerol⁶

c_1	c_2	c_3	c_4	c_5	c_6
13.5	0.8846	-1.150×10^{-3}	1.335×10^{-2}	3.78×10^{-1}	4.6×10^{-5}

equation, ΔT is calculated using the following equation:⁶

$$\Delta T/K = \{c_1 w_1 + c_2 w_1^2 + c_3 w_1^3\} \{c_4 \ln(p/kPa) + c_5\} [c_6 \{(p_0/kPa) - 1000\} + 1] \quad (2)$$

where w_1 , p , and p_0 are the concentration of the inhibitor in the aqueous phase (in mass fraction), the pressure of the system, and the dissociation pressure of fluid in the presence of distilled water at 273.15 K. The last term of eq 2, i.e. $c_6\{(p_0/kPa) - 1000\}$, describes the effect of the locus of the hydrate phase boundary of the fluid in the presence of distilled water.⁶ However, this term can be simply omitted with limited effect on the results.⁶ The constants c_i are given in the original manuscript for various inhibitors.⁶ These constants for glycerol are reported in Table 4.

In eq 1, T_0 can be calculated at any given pressure by using an appropriate predictive method such as the HWHYD thermodynamic model,⁸ which is capable of predicting different scenarios in hydrate phase equilibrium calculations. A detailed description of this model is given elsewhere.^{9,10} The model⁸ is briefly based on the equality of fugacity concept, which uses the Valderrama modification of the Patel–Teja equation of state¹¹ and nondensity dependent mixing rules¹² for modeling the fluid phases, and the van der Waals–Platteeuw theory¹³ is used for modeling the hydrate phase. This model,⁸ however, has not been developed for glycerol containing systems. As can be observed in the figures, the agreements between the experimental and predicted data are generally acceptable. However, the predictions of this correlation⁶ for dissociation conditions of propane simple hydrates in the presence of 0.1 mass fraction glycerol aqueous solution show some deviations from the experimental data (See Figure 3). These deviations were expected as the existing correlations reported in the literature¹ have generally been developed for methane-rich hydrocarbon systems and their applications for heavy hydrocarbons may be conservative.

4. Conclusions

Experimental dissociation data for methane, ethane, propane, and carbon dioxide simple hydrates in the presence of glycerol aqueous solutions with different concentrations of glycerol and at various temperatures (Table 1) were reported in this work. A reliable isochoric pressure-search method^{2–4} was used for performing all the measurements. The experimental data on dissociation conditions of carbon dioxide simple hydrates in the presence of 0.1 mass fraction glycerol aqueous solution were compared with the experimental data reported in the literature.⁵

The acceptable agreements between the experimental data measured in this work and the experimental data reported in the literature⁵ helped to confirm the reliability of the experimental technique and the data generated in this work. All the experimental data were finally compared with the predictions of a general correlation⁶ and acceptable agreements were generally found between the experimental and predicted data.

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