Hydrate Dissociation Pressures for Methane or Ethane in the Presence of Aqueous Solutions of Triethylene Glycol

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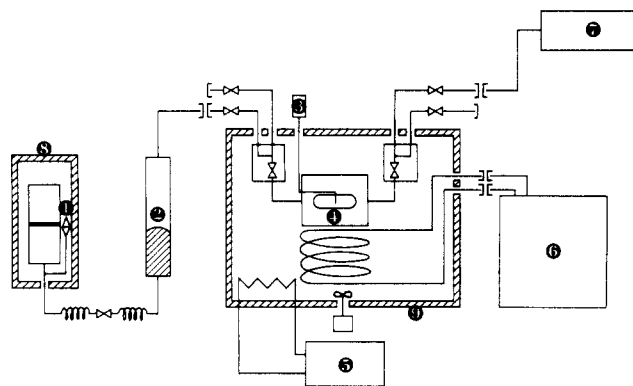BP Research Centre, Chertsey Road, Sunbury-on-Thames TW16 7LN, U.K.

Hydrate dissociation pressures for methane or ethane contacting aqueous solutions of triethylene glycol have been measured in the temperature range 273–294 K. A simple measurement technique is described which utilizes a high-pressure visual cell and is believed to be inaccurate to ±0.25 MPa in general, increasing to ±0.5 MPa at higher pressure.

Introduction

Hydrates are crystalline clathrate compounds that combine water and small gas molecules in the solid phase. The gas molecule is surrounded by a cage of water molecules, and the entire structure is stabilized by hydrogen bonding and van der Waals forces. The hydrate crystals resemble ice but are stable at much higher temperatures if the pressure of the system is raised. Unfortunately the fluids commonly found in the oil and gas industries readily form hydrates under favorable conditions. Unwanted hydrate formation during processing has motivated attempts to understand the chemical and physical properties of hydrate crystals and in particular their phase behavior so that occurrence can be avoided. The current state-of-the-art applied hydrate research has been reviewed by Sloan (1, 2).

The statistical model of the hydrate phase due to van der Waals and Platteeuw (3) or its more recent extensions (1, 2) are accepted as providing a sound basis for predicting hydrate phase equilibria to an accuracy sufficient for most engineering purposes. The hydrate model may be implemented, together with an equation of state or activity model for the fluid phases, in the manner suggested by Cole and Goodwin (4) to perform a rigorous multiphase flash calculation. One major advantage of this approach is the ability to accommodate the effects of hydrate inhibitors (such as glycols and alcohols) within the fluid phase model. The hitherto common use of a depression temperature equation, such as that proposed by Hammerschmidt (5), to correct the inhibitor free calculation of the hydrate phase boundary has been shown to be inaccurate at high concentrations of ethylene glycol and methanol in the aqueous phase (6). This method is less secure thermodynamically than an equation of state approach because of the nature of many of the assumptions used in its derivation (1, 7). The method is also cumbersome and not easily integrated into a process flow sheeting package (8).

Testing and quality assurance of predictive schemes requires a body of reliable experimental data. It is the purpose of this work to report new data for the hydrate phase boundary for pure methane or ethane contacting aqueous solutions of triethylene glycol. The experimental determination of the hydrate phase boundary is based on a very simple visual cell method in which the hydrate dissociation pressure is bracketed at constant temperature. A locus of dissociation pressure/temperature pairs serves to determine the hydrate phase boundary. The data reported in this work show that the method is not capable of the highest accuracy but is believed to be adequate for testing engineering calculations.

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Figure 1. Schematic diagram of the experimental apparatus: (1) pressure transducer; (2) gas bottle; (3) PRT; (4) visual cell; (5) PID temperature control; (6) recirculating cooler; (7) vacuum system; (8) positive displacement mercury pump; (9) stirred fluid bath.

Triethylene glycol is an inhibitor commonly employed in the oil and gas industries, but data concerning its efficacy appear to be absent from the open literature. It is expected that the results presented in this work will be of immediate benefit to those designing hydrate inhibition systems using triethylene glycol and those concerned with the prediction of hydrate phase equilibria with inhibitors present.

Experimental Section

Chemicals. The methane used for the present study was supplied by ECM special gases and had a stated purity of 99.99 mol %, as was the ethane which had a stated purity of 99.5 mol %. Triply distilled deionized water supplied by BDH was used throughout the study for gravimetric preparation of the aqueous phase in combination with dry triethylene glycol (TEG) obtained from Fluka AG with a stated purity of >99 mol %, molar mass of 150.8 g mol⁻¹, and density of 1.125 g cm⁻³.

Apparatus and Procedure. The experimental determination of hydrate phase boundaries is complicated by the occurrence of metastable fluid phase equilibria when crossing the hydrate phase boundary by cooling or raising the pressure in a cell. The hydrate formation conditions are not reproducible and are therefore unreliable estimates of the hydrate phase boundary. The hydrate dissociation conditions are reproducible, and therefore in this work the hydrate phase boundary is described by a locus of temperatures and corresponding hydrate dissociation pressures.

The isothermal apparatus shown schematically in Figure 1 was used for observing the formation and dissociation of
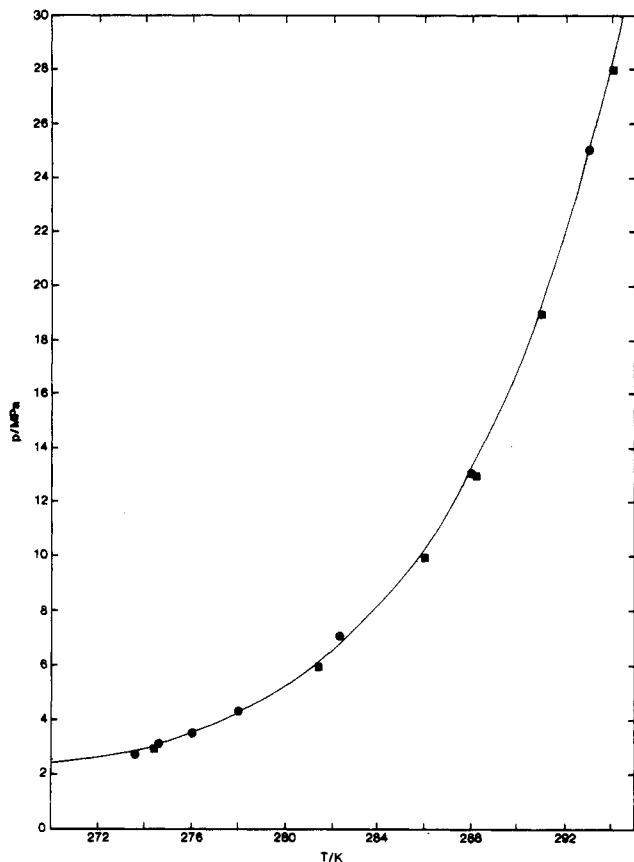
Figure 2. Dissociation pressure for binary methane/water system: ●, present data; ■, repeated data; —, best fit to present data.

hydrate crystals in the temperature range 273–294 K at pressures up to 41 MPa. A high-pressure visual cell (no. 4 in Figure 1) with internal volume of about 10 cm³ was mounted on a module and suspended in a well-insulated stirred fluid bath. The cell contents were agitated using manual rocking of the cell and allowing some mercury to move about, mixing the contents. The bath had a built-in window, and the cell contents were observed by back-lighting the cell and viewing through a telescope. The long-term temperature stability of the bath was believed to be of the order of ±10 mK.

The temperature of the cell contents was measured using a 100-Ω platinum resistance thermometer mounted inside the cell with an inaccuracy of ±0.1 K traceable via calibration to U.K. national standards (ITS-90). The experimental pressure was measured using a strain gauge type pressure transducer maintained at constant temperature in the positive displacement pump enclosure with an inaccuracy of ±20 kPa. The transducer was calibrated using a dead weight tester traceable to U.K. national standards. The fluids used for the study were stored in a titanium pressure vessel (internal volume 700 cm³) connected to the pressure cell with tubing of internal diameter approximately 0.8 mm. It was assumed that the thermal and material connection from the storage vessel to the visual cell does not affect the thermodynamic equilibrium with respect to the hydrate phase. The pressure of fluid in the storage vessel and cell could be held constant using the automatic positive displacement mercury pump.

Before beginning a set of measurements, the cell and all piping were cleaned with distilled water and solvents followed by evacuation for about 1.5 h. Then about 3 cm³ of the aqueous phase was introduced into the cell using a syringe, the balance of the cell volume was filled with mercury using the automatic pump, and the pressure was raised to that of the gas storage vessel. The cell and storage vessel pressures
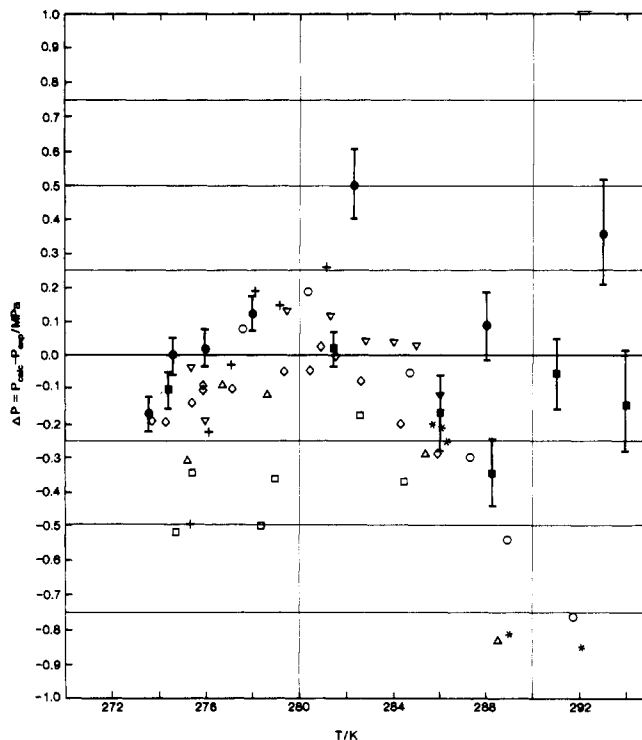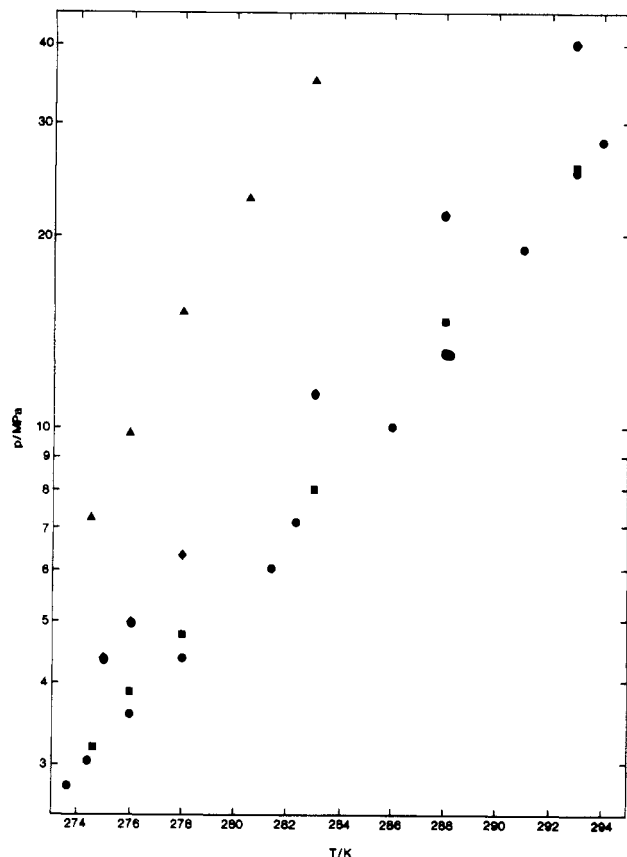

Figure 3. Dissociation pressure deviations from the correlation of eq 1: ●, present data; ■, repeated data; □, ref 6; ○, ref 9; ◊, ref 10; △, ref 11; ▽, ref 12; *, ref 13; +, ref 14.

Table I. Hydrate Dissociation Pressures for Methane and Aqueous Solutions of Triethylene Glycol

TEG concn/(wt %)	T/K	Δp/MPa	p/MPa
0.0	273.6	2.82–2.72	2.77
	274.6	3.22–3.12	3.17
	276.0	3.62–3.52	3.57
	278.0	4.42–4.32	4.37
	282.3	7.22–7.02	7.12
	288.0	13.22–13.02	13.12
	293.0	25.22–24.92	25.07
0.0 (repeat)	274.4	3.07–2.97	3.02
	281.4	6.07–5.97	6.02
	286.0	10.12–9.92	10.02
	288.2	13.12–12.92	13.02
	291.0	19.12–18.92	19.02
	294.0	28.22–27.82	28.02
10.0	274.6	3.22–3.12	3.17
	276.0	3.92–3.82	3.87
	278.0	4.82–4.72	4.77
	283.0	8.12–7.92	8.02
	288.0	14.82–14.62	14.72
	293.0	25.72–25.42	25.57
20.2	275.0	4.42–4.32	4.37
	276.0	5.02–4.92	4.97
	278.0	6.42–6.22	6.32
	283.0	11.42–11.22	11.32
	288.0	21.72–21.52	21.62
	293.0	40.02–39.72	39.87
40.0	274.5	7.32–7.22	7.27
	276.0	10.02–9.72	9.87
	278.0	15.52–15.02	15.27
	280.5	23.12–22.92	23.02
	283.0	35.32–35.02	35.17

were then equilibrated, and the cell was filled with gas by backing off the mercury. Once filled, the pressure in the cell and storage vessel was raised, using the automatic pump, until hydrates were formed. The formation of hydrates was facilitated by vigorous agitation of the cell during the pressure-raising stage. Once formed, the pressure was maintained and the cell left to equilibrate with occasional agitation for about 15 h. Subsequently the vessel and cell pressure was reduced in small stages with frequent agitation. The cell contents

Figure 4. Dissociation pressures for methane and aqueous solutions of triethylene glycol (TEG): ●, 0 wt % TEG; ■, 10 wt % TEG; ♦, 20.2 wt % TEG; ▲, 40 wt % TEG.

Table II. Hydrate Dissociation Pressures for Ethane and Aqueous Solutions of Triethylene Glycol

TEG concn/(wt %)	T/K	Δp/MPa	p/MPa
0.00	273.9	0.61–0.58	0.60
	278.1	0.98–0.95	0.96
	283.0	1.76–1.71	1.74
	288.0	5.72–5.62	5.67
	290.0	18.02–17.82	17.92
	292.0	32.52–32.42	32.52
10.0	277.0	1.02–0.99	1.00
	282.0	1.82–1.79	1.80
	286.3	3.82–3.62	3.72
	289.0	23.32–23.02	23.27
20.0	273.7	0.80–0.78	0.79
	276.5	1.30–1.28	1.29
	278.0	1.55–1.53	1.54
	283.0	2.64–2.62	2.63
	285.5	9.82–9.62	9.72
	288.0	28.42–28.12	28.27
	289.0	36.42–36.12	36.27
40.0	275.0	1.98–1.96	1.97
	275.8	2.31–2.28	2.30
	277.9	3.31–3.28	3.30
	281.7	21.02–20.52	20.77
	283.0	33.62–33.52	33.57

spent a period of about 30 min at each stage. The pressure steps used for each stage were chosen to be appropriate for the absolute pressure; therefore, at pressures of 20 or 30 MPa a pressure step of 100–300 kPa was used while at pressures below 1 MPa steps of about 30 kPa were selected. In this way the disappearance of the crystals and hence the hydrate phase boundary could be determined.

Results and Discussion

Hydrate dissociation pressures were obtained for methane and ethane in contact with aqueous triethylene glycol solutions
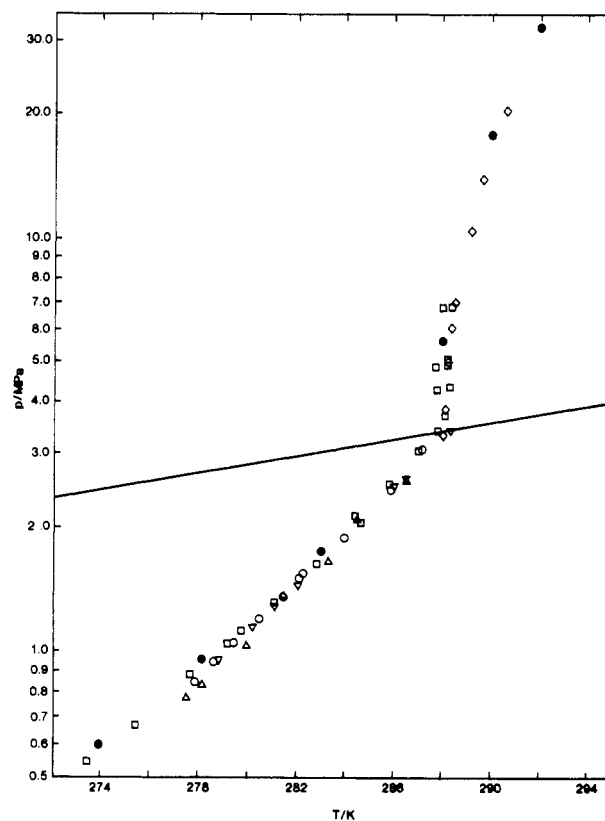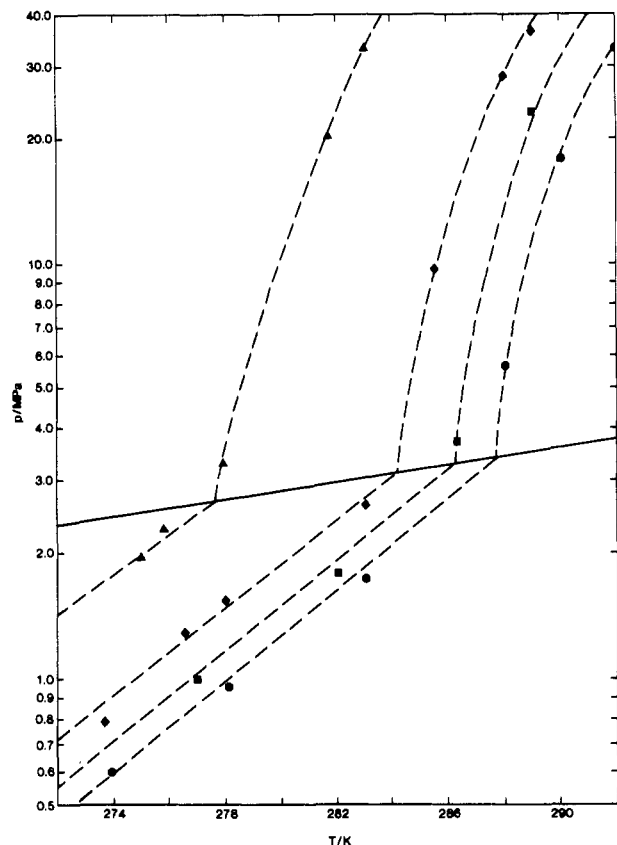

Figure 5. Dissociation pressures for the binary ethane/water system: ●, present data; ◊, ref 16; △, ref 17; □, ref 18; ○, ref 19; +, ref 20; —, vapor pressure, ref 15.

with concentrations of 0, 10, 20, and 40 wt %. The reported pressure is the mean pressure, p, for the step, during which the hydrate crystals disappeared.

Methane. The complete set of new results for methane is presented in Table I. The data for methane and pure water comprise two sets obtained over a year apart with different fluid charges. Both sets are shown graphically in Figure 2 where the dissociation pressure, p, is plotted against temperature, T. The repeated data deviate by no more than 0.7 MPa from the best fit curve to the original set with a mean systematic deviation of –0.4 MPa. To compare the present data with previous work, the dissociation pressure and temperature from both sets were correlated using standard nonlinear fitting techniques to obtain the equation

$$p/\text{MPa} = 1.51 + (T/271.2\text{K})^{40.67} \tag{1}$$

Figure 3 shows the deviation, Δp, from the correlation of eq 1 of the new data and a selection of earlier measurements obtained in the same temperature range (6, 9–14). The standard deviation of the fit to the new data is 0.25 MPa with a maximum deviation of about 0.5 MPa. These figures are generally larger than would be expected to be entirely consistent with the pressure steps used to bracket the phase boundary and the claimed accuracy of the cell temperature measurement. However, when compared with earlier work, the new data show broad agreement, with most data points lying within 1 standard deviation (0.25 MPa) of the correlation (which reflects the general level of scatter in the entire data set). A notable exception to this are the measurements of Song and Kobayashi (6) at low temperatures which deviate by about 0.5 MPa below the correlation. The reason for this remains obscure. The deviation plot and repeatability study indicate that the data reported in this work are inaccurate at the level of ±0.25 MPa, increasing to about ±0.5 MPa at the highest pressures.

Figure 6. Dissociation pressures for ethane and aqueous solutions of triethylene glycol (TEG): ●, 0 wt % TEG; ■, 10 wt % TEG; ◆, 20 wt % TEG; ▲, 40 wt % TEG.

Figure 4 shows the entire new data set for methane. The curves for 10 and 20 wt % triethylene glycol are essentially parallel to the inhibitor free curve, but at the highest concentration of 40 wt % this is not the case. This behavior has been observed by Song and Kobayashi (6) in their work with aqueous ethylene glycol and methanol solutions. There appear to be no data in the open literature for methane and aqueous solutions of triethylene glycol, so no comparison is possible.

Ethane. The new data set for ethane and aqueous triethylene glycol systems is presented in Table II. The set includes results for ethane in both gas and liquid phases. The data for ethane and pure water are shown graphically in Figure 5 along with a selection of earlier data (*16–20*) which are

broadly in agreement with the present set. Also included is the saturated vapor pressure line for pure ethane calculated using the equation recommended by Reid, Prausnitz, and Poling (*15*). At high pressures, in the liquid phase, the hydrate dissociation pressure increases rapidly with small changes in temperature.

The entire ethane data set is presented in Figure 6, which also shows the calculated saturation pressure curve. The dashed lines in Figure 6 were graphically constructed to clarify and differentiate the data sets. The lines are not the result of curve fits and should not be interpreted as having any physical significance. There appear to be no data in the open literature with which to compare the present set, and more data is needed before a detailed thermodynamic analysis is warranted.

Acknowledgment

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