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## Accepted Manuscript

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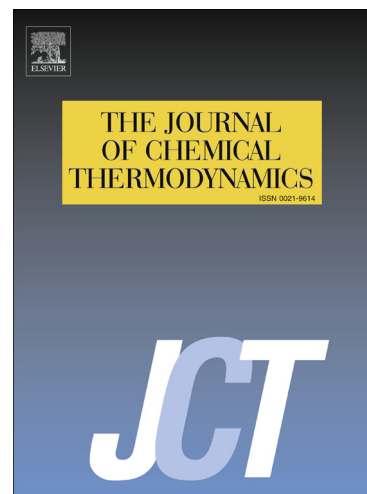
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# Gas Hydrate Equilibria in the Presence of Monoethylene Glycol, Sodium Chloride and Sodium Bromide at Pressures up to 150 MPa

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## KEYWORDS

Gas Hydrates; Monoethylene glycol; High pressure; Sodium Chloride, Sodium Bromide,

## ABSTRACT

Hydrate dissociation data for single hydrate formers are widely available, however there is a clear gap for multicomponent systems over a wide range of pressures and in presence of inhibitor or electrolytes. This data is required to validate thermodynamic models being used to predict hydrate inhibitor (monoethylene glycol (MEG)) requirements in pipelines transporting unprocessed well streams with highly concentrated formation waters and, in the

case of sodium bromide, drilling fluids. In this work, hydrate dissociation temperature measurements at pressures up to 150 MPa were conducted for a multicomponent synthetic gas mixture in equilibrium with deionised water, an aqueous sodium chloride solution, mixed aqueous MEG /sodium chloride and MEG / sodium bromide solutions using the isochoric step heating method.

The Soave-Redlich and Kwong - Cubic-Plus-Association equation of state combined with a modified Debye Hückel electrostatic term is employed to model the phase equilibria. The hydrate-forming conditions are modelled by the solid solution theory of van der Waals and Platteeuw. The thermodynamic model has been evaluated using these new generated hydrate data. The thermodynamic model (as implemented in our in-house software HWPVT 1.1) and experimental data are in good agreement, supporting the reliability of the developed model.

## 1. Introduction

A thorough assessment of potential flow assurance issues is essential in order to develop a reliable strategy for initial and future development of any field. In cases where untreated reservoir fluids encounter low temperatures combined with high pressures, hydrate formation is a high possibility. In some cases there may be a strong tendency for the hydrates to adhere to pipeline walls restricting flow and potentially leading to blockage. As removal of hydrate plugs can be challenging, leading to potential safety issues and expensive delays, prevention is a high priority. Continuous injection of MEG is a commonly used approach, shifting the hydrate formation temperature lower than will be encountered at any point in the pipeline. In order to ensure that the MEG injection rates are sufficient to avoid hydrate formation a reliable thermodynamic model is required that has been validated using accurate experimental data. Hydrate data are widely available for single hydrate formers with moderate concentrations of salts and thermodynamic inhibitors, however there is limited data

available for realistic multi-component gas mixtures with high concentrations of MEG and combinations of MEG and salts [1]. In this work, hydrate dissociation temperature measurements were made at pressures up to 150 MPa for a multicomponent synthetic gas mixture in equilibrium with deionised water, a 25 wt% aqueous sodium chloride solution and mixed aqueous MEG /sodium chloride solutions.

The potential for hydrate formation in water based drilling fluids must be considered especially where high pressures / low temperatures may be encountered. There is limited data for some of the salts commonly used at high concentrations in drilling fluids in combination with MEG that can be used for model validation purposes. In this work, hydrate dissociation temperature measurements were made at pressures up to 150 MPa for a multicomponent synthetic gas mixture in equilibrium with a 40 wt% aqueous sodium bromide solution and a mixed aqueous MEG /sodium bromide solution.

A thermodynamic approach, in which the Cubic-Plus-Association equation of state is combined with a modified Debye Hückel electrostatic term, has been employed to model the phase equilibria. To take into account the salt–MEG interactions, a binary parameter was introduced in the modified Debye Hückel electrostatic term. The hydrate-forming conditions are modelled by the solid solution theory of van der Waals and Platteeuw. A complete description of the model (HWPVT 1.1) can be found in [1–3].

## **2. Experimental equipment**

Two different types of experimental set-up were used to make the hydrate dissociation temperature measurements, as detailed below.

*Mixed Autoclave Rig (MAR)*

2 different mixed autoclave rigs with different volumes (420 and 467 ml) were used in this work. The basic rig design is comprised of a high pressure cell fitted with a magnetic mixer with a maximum rotation speed of 1,500 revolutions per minute giving good mixing of the cell contents. The rig is surrounded by a jacket through which coolant is circulated using a refrigerated circulator. The rig is well insulated and can be used at temperatures in the range of 233 to 333 K and at pressures up to 41 MPa. The pressure is measured using a strain gauge pressure transducer with an accuracy of  $u(P) = 0.02$  MPa. The temperature is measured using a Platinum Resistance Temperature (PRT) Probe with an accuracy of  $u(T) = 0.1$  K.

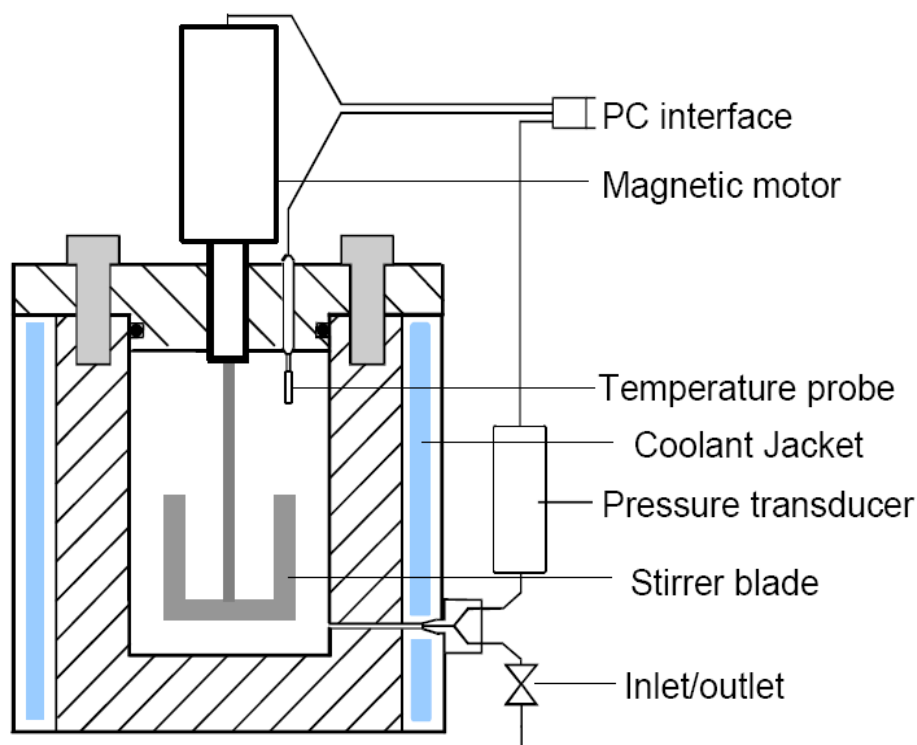


Figure 1. Schematic of hydrate mixed autoclave rig.

*High Pressure Rocking Rig (HPRR)*

The high pressure rocking rig is comprised of a small volume (35 ml) cell with an inbuilt jacket for circulating fluid from a constant temperature circulator. The experimental rig can be used at pressures up to 200 MPa. A high pressure PRT probe is mounted on the cell so that the sensing part is in the centre of the cell in contact with the test fluids. The accuracy of the temperature measurement is  $u(T) = 0.1$  K. A *Quartzdyne* pressure transducer mounted outside the cell is used to measure the pressure. The accuracy of the pressure measurement is  $u(P) = 0.05$  MPa. A schematic of the equilibrium cell is shown in Figure 2. The equilibrium cell is mounted on a compressed air driven rocking mechanism allowing the cell contents to be mixed continuously during a test. Steel ball bearings are also placed in the equilibrium cell in order to improve the mixing efficiency. A constant temperature circulator is used to control the cell temperature.

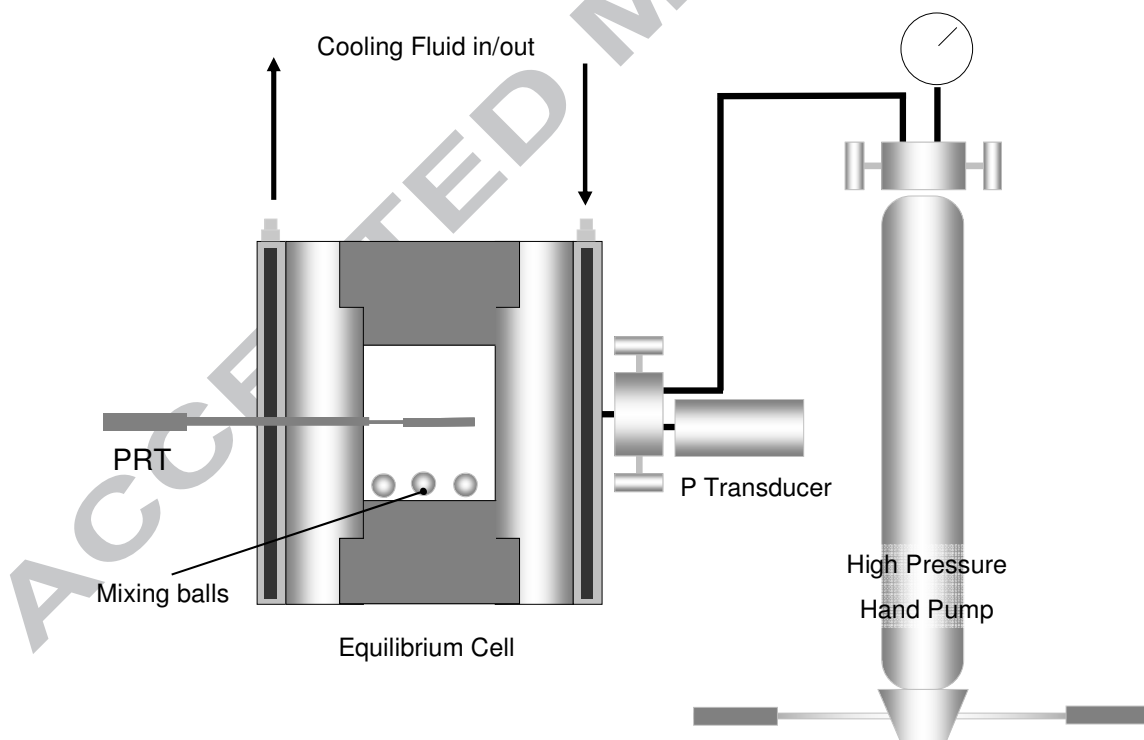


Figure 2. Schematic high pressure rocking rig.

For all of the experimental set-ups used in this work:

- The temperature and pressure are recorded using a PC.
- The temperature probes are regularly calibrated against a platinum resistance probe that has a certificate of calibration issued in accordance with NAMAS Accreditation Standard and NAMAS Regulations.
- The pressure transducers are calibrated and checked using a Budenberg dead weight tester.
- The accuracy and reliability have been checked by comparing experimental data generated with these rigs with data both from literature and those measured previously by The Centre for Hydrate Research, Institute of Petroleum Engineering, Heriot-Watt University.

### **3. Experimental methods**

Dissociation temperature measurements were made using the isochoric step-heating method [4,5]. In this method the cell is charged with a measured weight of aqueous fluid and then pressurised with the hydrocarbon system to the desired starting pressure. The temperature is then lowered to form hydrates, growth being detected by an associated drop in the cell pressure (as gas becomes trapped in hydrate structures). The cell temperature is then raised step-wise (~1 K steps), allowing enough time at each temperature step for equilibrium to be reached. At temperatures below the point of complete dissociation, gas is released from decomposing hydrates, giving a marked rise in the cell pressure with each temperature step. However, once the cell temperature has passed the final hydrate dissociation point, and all clathrates have disappeared from the system, a further rise in the temperature will result only in a relatively small pressure rise due to thermal expansion. This process results in two traces



with different slopes on a pressure versus temperature ( $P/T$ ) plot, one before and one after the dissociation point. The point where these two traces intersect (i.e., an abrupt change in the slope of the  $P/T$  plot) is taken as the dissociation point. An example of a dissociation point measurement is shown in Figure 3.

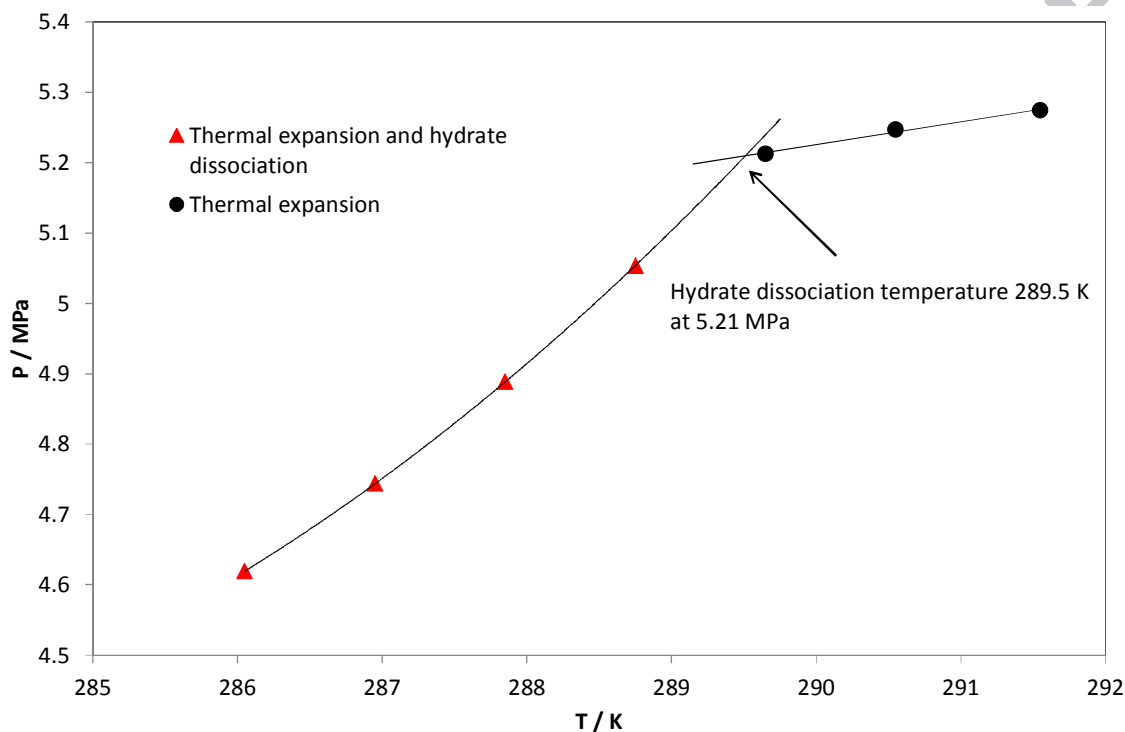


Figure 3. Example of hydrate dissociation temperature measurement using plot of equilibrium temperatures and pressures in a test with multi-component gas mixture (Table 1) and deionised water.

#### 4. Experimental materials

The composition of the multi-component gas mixture as measured by GC is given in Table 1. Deionised water was used in all tests and aqueous solutions were made by gravimetric means. The MEG, NaBr and NaCl purities were stated as 99.5% pure. The mass of salt and MEG were determined using a Mettler Toledo balance (model PB3002) with a resolution of 0.001 g

and thus, the relative uncertainty in the concentration of the NaCl /NaBr/MEG in aqueous solutions is taken equal to the purity of the salt or chemical (0.5 %).

The concentration of the solutions is given in terms of the concentration of salt or glycol with respect to pure water. Hence for the mixture with 20 wt% NaCl and 30 wt% MEG the weight of NaCl divided by the weight of pure water + weight of NaCl = 0.2, and the weight of MEG divided by the weight of pure water + weight of MEG = 0.3.

Table 1. Multi-component gas composition (mole fraction) as certified by BOC.

Component	x	U(k=2,x)
N <sub>2</sub>	0.0219	0.00044
CO <sub>2</sub>	0.0228	0.00046
C <sub>1</sub>	0.8598	0.01720
C <sub>2</sub>	0.0509	0.001018
C <sub>3</sub>	0.0396	0.000792
<i>i</i> C <sub>4</sub>	0.0016	0.000032
<i>n</i> C <sub>4</sub>	0.0026	0.000052
<i>i</i> C <sub>5</sub>	0.0004	0.000008
<i>n</i> C <sub>5</sub>	0.0004	0.000008

Table 2. Suppliers and specification as stated by the supplier of the materials used in this work.

Chemical name	Supplier	Mass fraction purity
Deionised Water	Pure Lab Elga 2	-
Sodium Chloride	Fischer Scientific	>0.995
Sodium Bromide	Fischer Scientific	>0.995
MEG	Sigma-Aldrich	>0.995

## 5. Results

The hydrate dissociation temperature measurements for hydrates formed from the multi-component gas mixture (Table 1) with deionised water are shown in Table 3 and plotted in Figure 4 along with the model predictions. Experimental data at pressure above 50 MPa are not widely available for comparison, therefore the results for distilled water are compared against similar natural gases at a lower pressure range (Figure 5). For all these examples, the model can predict the dissociation conditions well within the reported experimental error ( $T < 0.5$  K). The measurements with 25 wt% NaCl are presented in Table 4. The measurements in the presence of aqueous solutions composed of 30, 40, and 50 wt% MEG all with 20 wt% NaCl are given in Tables 5 through 7. The measurements in the presence of 40 wt% NaBr and 40 wt% NaBr/40 wt% MEG are given in Tables 8 and 9. Details of the rig and aqueous solution loaded are given for all tests apart from those with deionised water.

Table 3. Hydrate dissociation temperatures for multi-component gas (Table 1) with deionised water.

Rig type	T / K <sup>a</sup>	P / MPa	T <sub>pred</sub> / K	$\Delta T^d$ / K
MAR	289.6	5.21 <sup>b</sup>	289.3	0.3
MAR	293.9	10.1 <sup>b</sup>	293.5	0.4
MAR	296.5	20.36 <sup>b</sup>	296.8	-0.3
HPRR	305.9	74.37 <sup>c</sup>	306.0	-0.1
HPRR	313.4	139.44 <sup>c</sup>	313.7	-0.3
			$\Delta T_a$	<b>0.3</b>

$${}^a u(T)=0.1 \text{ K} \quad {}^b u(P)=0.02 \text{ MPa} \quad {}^c u(P)=0.05 \text{ MPa} \quad {}^d \Delta T= T-T_{\text{pred}}$$

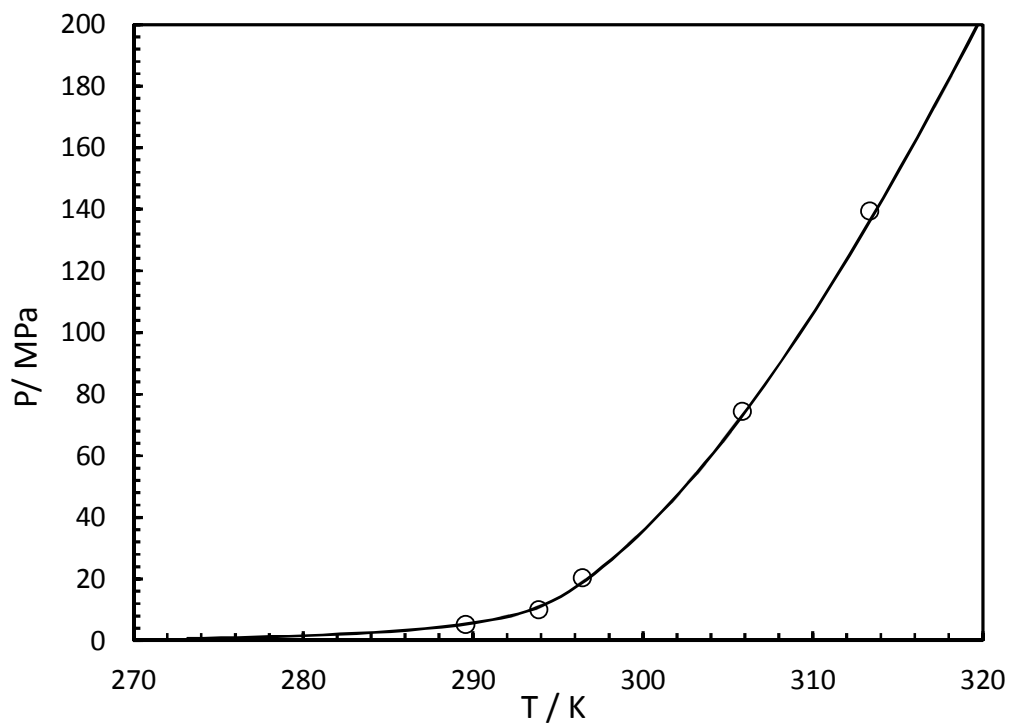


Figure 4. Experimental hydrate dissociation point data and predicted hydrate phase boundaries for hydrates formed from a multi-component gas mixture (Table 1) in the presence of deionised water.

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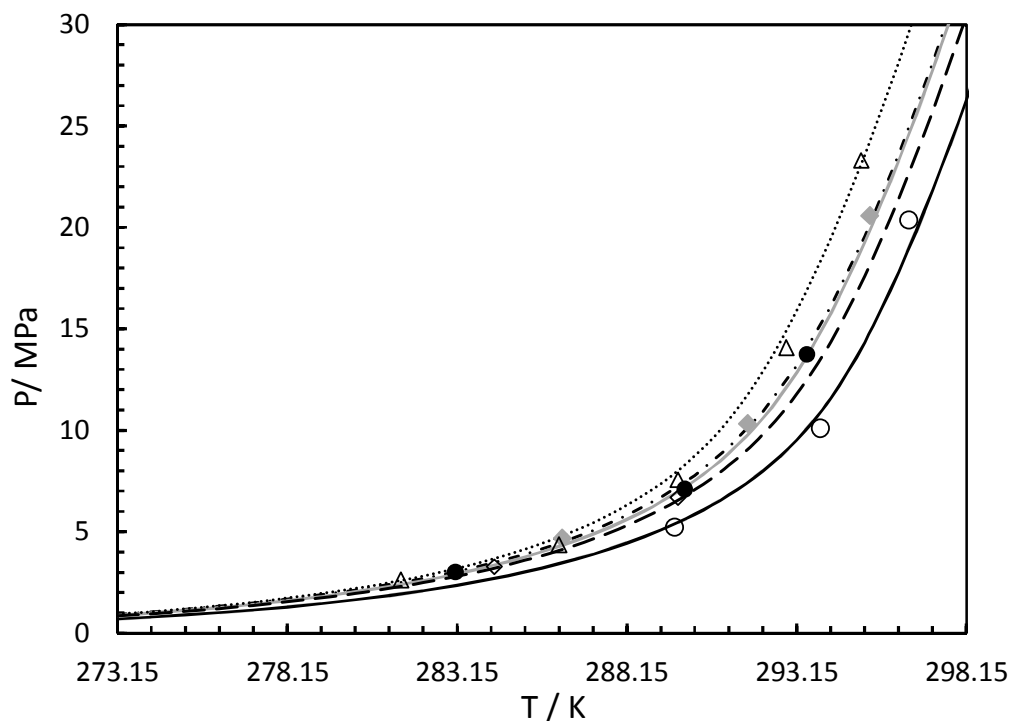


Figure 5. Experimental hydrate dissociation point data and predicted hydrate phase boundaries for hydrates formed from multi-component gas mixtures in the presence of deionised water. ○, this work (— predictions); △, N<sub>2</sub>: 5.96, CO<sub>2</sub>: 14.19, CH<sub>4</sub>: 71.60, C<sub>2</sub>H<sub>6</sub>: 4.73, C<sub>3</sub>H<sub>8</sub>: 1.94, nC<sub>4</sub>H<sub>10</sub>: 0.79, nC<sub>5</sub>H<sub>12</sub>: 0.79 (••• predictions) [6]; ●, N<sub>2</sub>: 2.24, CO<sub>2</sub>: 2.33, CH<sub>4</sub>: 88.06, C<sub>2</sub>H<sub>6</sub>: 5.21, C<sub>3</sub>H<sub>8</sub>: 1.64, iC<sub>4</sub>H<sub>10</sub>: 0.16, nC<sub>4</sub>H<sub>10</sub>: 0.27, iC<sub>5</sub>H<sub>12</sub>: 0.04, nC<sub>5</sub>H<sub>12</sub>: 0.05 (- · - predictions) [6]; ◆, N<sub>2</sub>: 7.0, CH<sub>4</sub>: 84.13, C<sub>2</sub>H<sub>6</sub>: 4.67, C<sub>3</sub>H<sub>8</sub>: 2.34, nC<sub>4</sub>H<sub>10</sub>: 0.93, nC<sub>5</sub>H<sub>12</sub>: 0.93 (— predictions) [6]; ●, N<sub>2</sub>: 1.50, CO<sub>2</sub>: 2.13, CH<sub>4</sub>: 87.44, C<sub>2</sub>H<sub>6</sub>: 6.00, C<sub>3</sub>H<sub>8</sub>: 2.43, iC<sub>4</sub>H<sub>10</sub>: 0.20, nC<sub>4</sub>H<sub>10</sub>: 0.30 (- - - predictions) [7].

Table 4. Hydrate dissociation temperatures for multi-component gas (Table 1) in the presence of 25 wt% NaCl ( $u(w_{\text{NaCl}})=0.125\text{wt}\%$ ).

Rig details				Hydrate dissociation conditions			
Rig type	Rig volume / ml	Aqueous solution / g	Gas mixture / g	T/ K <sup>a</sup>	P / MPa	T <sub>pred</sub> / K	$\Delta T^d$ / K
MAR	467	271.1	12.8	273.1	4.97 <sup>b</sup>	273.3	-0.2
MAR			57.4	277.8	19.6 <sup>b</sup>	279.4	-1.6
MAR	420	371.9	36.5	285.1	68.48 <sup>b</sup>	286.8	-1.7
HPRR	35	15.0	8.65	293.6	146.38 <sup>c</sup>	294.9	-1.3
						$\Delta T_a$	<b>1.2</b>

$${}^a u(T)=0.1 \text{ K } {}^b u(P)=0.02 \text{ MPa } {}^c u(P)=0.05 \text{ MPa } {}^d \Delta T= T-T_{\text{pred}}$$

Table 5. Hydrate dissociation temperatures for multi-component gas (Table 1) in the presence of 20 wt% NaCl ( $u(w_{\text{NaCl}})=0.1\text{wt}\%$ ) and 30 wt% MEG ( $u(w_{\text{MEG}})=0.15\text{wt}\%$ ), both with respect to pure water. The weight of NaCl divided by the weight of pure water + weight of NaCl = 0.2, and the weight of MEG divided by the weight of pure water + weight of MEG = 0.3.

Rig details				Hydrate dissociation conditions			
Rig type	Rig volume / ml	Aqueous solution / g	Gas mixture / g	T/ K <sup>a</sup>	P / MPa <sup>b</sup>	T <sup>pred</sup> / K	$\Delta T^c$ / K
MAR	467	413.7	27.6	269.7	4.96	268.5	1.2
MAR			53.6	273.7	20.67	274.3	-0.6
MAR	420	419.6	22.4	280.5	68.18	281.6	-1.1
						$\Delta T_a$	<b>1.0</b>

$${}^a u(T)=0.1 \text{ K } {}^b u(P)=0.02 \text{ MPa } {}^c \Delta T= T-T_{\text{pred}}$$

Table 6. Hydrate dissociation temperatures for multi-component gas (Table 1) in the presence of 20 wt% NaCl ( $u(w_{\text{NaCl}})=0.1\text{wt}\%$ ) and 40 wt% MEG ( $u(w_{\text{MEG}})=0.2\text{wt}\%$ ), both with respect to pure water. The weight of NaCl divided by the weight of pure water + weight of NaCl = 0.2, and the weight of MEG divided by the weight of pure water + weight of MEG = 0.4.

Rig details				Hydrate dissociation conditions			
Rig type	Rig volume / ml	Aqueous solution / g	Gas mixture / g	T/ K <sup>a</sup>	P / MPa	T <sup>pred</sup> / K	$\Delta T^d$ / K
MAR	467	376.7	8.1	265.4	5.09 <sup>b</sup>	265.2	0.2
MAR			34.4	269.9	19.92 <sup>b</sup>	270.3	-0.4
MAR	420	425.4	22.4	276.5	68.55 <sup>b</sup>	277.7	-1.2
HPRR	35	15.0	8.68	286.1	142.10 <sup>c</sup>	285.9	0.2
						$\Delta T_a$	<b>0.5</b>

$${}^a u(T)=0.1 \text{ K} \quad {}^b u(P)=0.02 \text{ MPa} \quad {}^c u(P)=0.05 \text{ MPa} \quad {}^d \Delta T= T-T_{\text{pred}}$$

Table 7. Hydrate dissociation temperatures for multi-component gas (Table 1) in the presence of 20 wt% NaCl ( $u(w_{\text{NaCl}})=0.1\text{wt}\%$ ) and 50 wt% MEG ( $u(w_{\text{MEG}})=0.25\text{wt}\%$ ), both with respect to pure water. The weight of NaCl divided by the weight of pure water + weight of NaCl = 0.2, and the weight of MEG divided by the weight of pure water + weight of MEG = 0.5.

Rig details				Hydrate dissociation conditions			
Rig type	Rig volume / ml	Aqueous solution / g	Gas mixture / g	T/ K <sup>a</sup>	P / MPa	T <sup>pred</sup> / K	$\Delta T^d$ / K
MAR	467	317.7	9.9	259.4	5.13 <sup>b</sup>	260.3	0.9
MAR			46.1	263.6	20.00 <sup>b</sup>	264.8	1.2
MAR	420	413.9	13.53	271.3	69.84 <sup>b</sup>	272.4	1.1
HPRR	35	15.0	8.74	278.1	139.45 <sup>c</sup>	280.3	2.2

						$\Delta T_a$	<b>1.3</b>
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$${}^a u(T)=0.1 \text{ K } {}^b u(P)=0.02 \text{ MPa } {}^c u(P)=0.05 \text{ MPa } {}^d \Delta T= T-T_{\text{pred}}$$

Table 8. Hydrate dissociation temperatures for multi-component gas (Table 1) in the presence of 40 wt% NaBr ( $u(w_{\text{NaBr}})=0.2\text{wt}\%$ ).

Rig details				Hydrate dissociation conditions			
Rig type	Rig volume / ml	Aqueous solution / g	Gas mixture / g	T/ K <sup>a</sup>	P / MPa <sup>b</sup>	T <sup>pred</sup> / K	$\Delta T^c$ / K
MAR	467	410.3	9.8	269.2	4.94	267.1	2.1
MAR			24	273.7	19.75	272.3	1.4
MAR	420	527.6	21.2	280.3	66.86	279.7	0.6
						$\Delta T_a$	<b>1.4</b>

$${}^a u(T)=0.1 \text{ K } {}^b u(P)=0.02 \text{ MPa } {}^c \Delta T= T-T_{\text{pred}}$$

Table 9. Hydrate dissociation temperatures for multi-component gas (Table 1) in the presence of 40 wt% NaBr ( $u(w_{\text{NaBr}})=0.2\text{wt}\%$ ) and 40 wt% MEG ( $u(w_{\text{MEG}})=0.2\text{wt}\%$ ), both with respect to pure water. The weight of NaBr divided by the weight of pure water + weight of NaBr = 0.4, and the weight of MEG divided by the weight of pure water + weight of MEG = 0.4.

Rig details				Hydrate dissociation conditions			
Rig type	Rig volume / ml	Aqueous solution / g	Gas mixture / g	T/ K <sup>a</sup>	P / MPa <sup>b</sup>	T <sup>pred</sup> / K	$\Delta T^c$ / K
MAR	467	212.74	8.5	259.4	5.13	257.8	1.6
MAR		450.23	37.1	262.3	19.77	261.8	0.5
MAR	420	490.53	24	269.4	69.51	269.3	0.1



						$\Delta T_a$	0.7
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$${}^a u(T)=0.1 \text{ K} \quad {}^b u(P)=0.02 \text{ MPa} \quad {}^c \Delta T= T-T_{\text{pred}}$$

The hydrate dissociation temperature measurements for tests with deionised water, 25 wt% NaCl and aqueous solutions composed of 30, 40, and 50 wt% MEG all with 20 wt% NaCl are plotted together in Figure 6 along with model predictions. As can be seen the agreement between experimental data and the predicted hydrate stability zone is excellent in the case of deionised water and good for all other systems with a maximum deviation of 1 °C.

The hydrate dissociation temperature measurements for tests with deionised water, 40 wt% NaBr and 40 wt% NaBr and 40 wt% MEG are plotted together in Figure 7 along with model predictions. As can be seen the agreement between experimental data and the predicted hydrate stability zone is good for the NaBr and NaBr/MEG aqueous solutions with a maximum deviation of 1 °C.

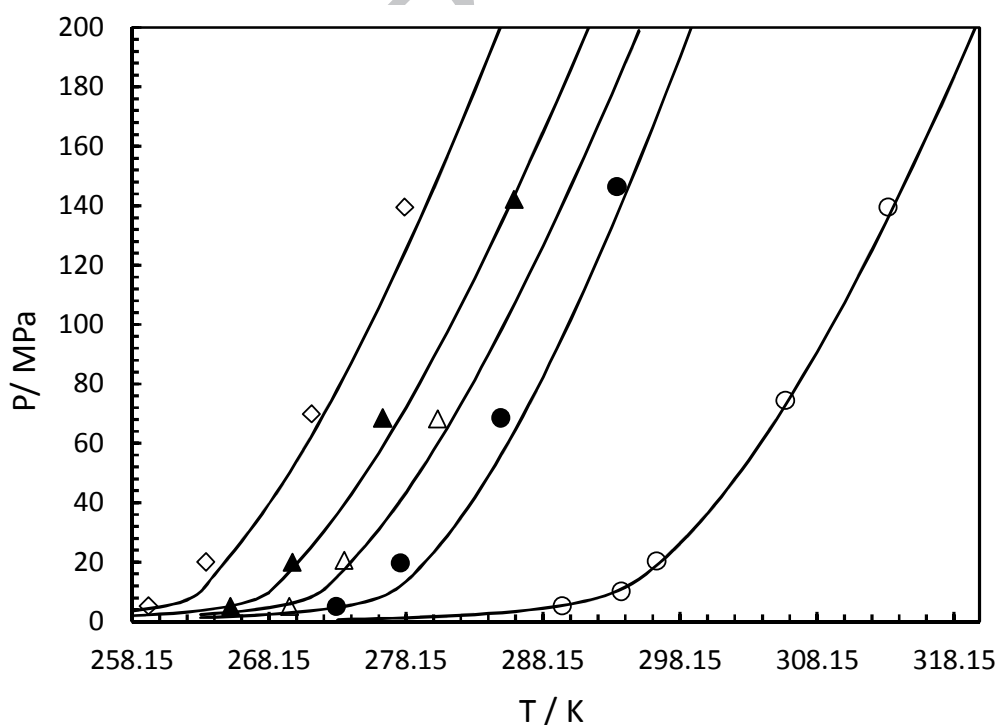


Figure 6. Experimental hydrate dissociation point data and predicted hydrate phase boundaries for hydrates formed from a multi-component gas mixture (Table 1) in the presence of ○: deionised water; ● : 25 wt% NaCl; △: 20 wt% NaCl and 30 wt% MEG; ▲: 20 wt% NaCl and 40 wt% MEG; ◇: 20 wt% NaCl and 50 wt% MEG; Solid lines are predictions. All NaCl and MEG concentrations are with respect to pure water.

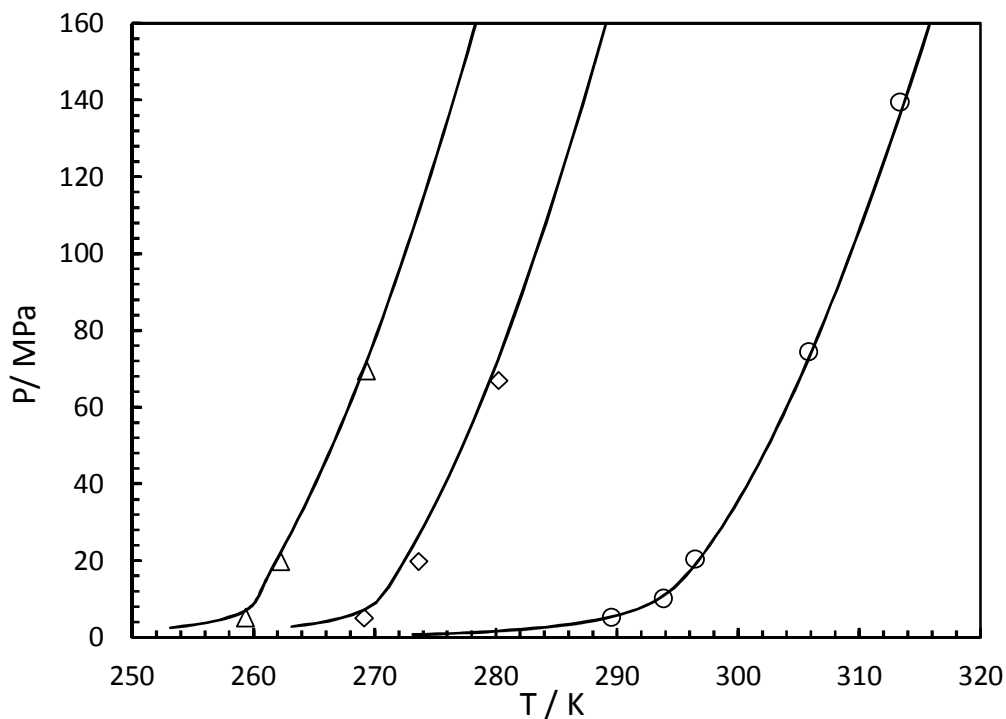


Figure 7. Experimental hydrate dissociation point data and predicted hydrate phase boundaries for hydrates formed from a multi-component gas mixture (Table 1) in the presence of ○ : deionised water; ◇: 40 wt% NaBr; △: 40 wt% NaBr and 40 wt% MEG, both with respect to pure water. Solid lines are predictions.

## 6. Conclusions

The experimental data presented in this paper provides valuable data that can be used to validate predictions of thermodynamic models used to predict hydrate stability zones for systems with high concentrations of salts and thermodynamic inhibitors, at pressures up to

150 MPa. There is good agreement between the experimental data and model (HWPVT) predictions, made using the Soave-Redlich and Kwong -Cubic-Plus-Association equation of state. As the experimental data was not used to tune the model, it can be considered as independent, and therefore this agreement provides validation of the modelling approach for systems with a wide range of concentrations of salts and thermodynamic inhibitors.

### Acknowledgements

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## Highlights

Paper provided new experimental data with high concentrations of salts and thermodynamic inhibitors, at pressures up to 150 MPa.

Good agreement between the experimental data and model (HWPVT) predictions, made using the Soave-Redlich and Kwong -Cubic-Plus-Association equation of state.

This agreement provides validation of the modelling approach for systems with a wide range of concentrations of salts and thermodynamic inhibitors.

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