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GLYCOLS PARTITIONING AT HIGH PRESSURES IN GAS PROCESSING SYSTEMS

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ABSTRACT

Glycols are commonly used chemicals in the gas processing industry, for example monoethylene glycol is (MEG) injected at the well head to prevent hydrate formation; glycols are also used in dehydration units to remove water from natural gas streams. Because of the low vapour pressure of glycols, limited information on glycol solubility in high pressure systems is available in the literature.

In this work, a new experimental approach is presented to determine the water and glycols concentration in high pressure gas streams. The method uses a Tuneable Diode Laser Absorption Spectroscopy (TDLAS) sensor for water detection combined with Thermal Desorption Gas Chromatography for the analysis of glycols. The setup was initially tested by measuring pure glycol solubility in methane. Water content measurements were also carried out for glycol solutions over a wide range of temperature and pressure and finally gas solubility in pure glycols and aqueous solutions were measured to tune the thermodynamic mode. The Cubic Plus Association (CPA) equation of state adjusted on experimental solubility data was used to model the distribution of glycols and water in the gas phase.

Keywords: Methane; Natural Gas; Phase Behaviour; MEG; TEG.

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GLYCOLS PARTITIONING AT HIGH PRESSURES IN GAS PROCESSING SYSTEMS

INTRODUCTION

Glycols are chemicals commonly used in many commercial and industrial applications including antifreeze, cryo-conservation and coolant. They also are used as raw materials in the production of a wide range of products. Glycols are extensively used in the oil and gas industry, particularly for gas dehydration and hydrate prevention.

Glycols can be typically used for applications where dew point depressions up to 70°C are required and to prevent hydrate formation in unprocessed streams at concentrations up to 70 wt% (to water). Monoethylene glycol (MEG) is often used to avoid hydrate formation and in many new developments, MEG is the preferred hydrate inhibitor over methanol. Another application where glycols are of importance is during the drying of natural gases where TEG is generally the preferred solvent.

In this communication we present experimental techniques, equipment and thermodynamic modelling for investigating the phase behaviour of hydrocarbons – glycol systems with and without water.

The thermodynamic modelling is based on the cubic-plus-association equation of state (CPA EoS) for fugacity calculations in all phases, which have been used to model the fluid phases with previously reported binary interaction parameters [1,2].

In this communication, some examples of experimental measurements for MEG and TEG systems are reported. New experimental solubility measurements of methane in pure MEG, TEG and aqueous solutions over a wide range pressures and temperatures were investigated. New experimental measurements are reported for the glycol (MEG and TEG) content data of methane and used for evaluation of the model. The results of the predictions are compared with experimental data, demonstrating reliability of the techniques developed in this work

EXPERIMENTAL SETUP AND PROCEDURES

A schematic of the set-up used for the solubility study is shown in Figure 1. The apparatus used in this work was the same as the setup used by Chapoy et al. [3] and Wise et al. [4] to measure the saturation pressure of a multicomponent high CO₂ mixture and solubility of CO₂ in TEG, respectively.

The 350 cm³ (piston-less) pressure rocking cell was loaded with 300 cm³ of glycol solution via the top keeping the cell horizontal. The rocking cell was then sealed. A vacuum pump was connected to V02, removing the air from the rocking cell, thus minimising the interference of air in the solubility measurements. Methane was injected into the rocking cell from a purge line. The line was then disconnected from V02. The pneumatic rocking system was used to agitate the mixture until the system demonstrated a steady pressure and temperature on the logger, ensuring equilibrium was reached.

A number of steps were required during each solubility measurement. Firstly, the pneumatic rocking system was disabled, and the rocking cell was locked in a vertical position. The methane cylinder was then connected to the rocking cell (V02), the flash tank was connected using V03 and the VINCI Technology manual gas cylinder was connected to the flash tank (V05).

During each measurement the pressure and temperature of the cell, together with the pressure, temperature and initial volume of the gas meter chamber were recorded. The pressure of the cell in the rig was kept constant during sampling by methane injection (V02) from the methane pressure cell. A liquid sample (average of 21 grams per run) was then flashed. The volume of the gas together with the sample weight was then recorded. The density of methane at each sampling condition (calculated using the GERG equation of state) was used to determine the moles of methane. These were used to calculate the solubility of methane in TEG/solution. The pressure of the cell was increased by methane injection from V01 and V02 and the procedure repeated, producing solubility results at various pressures and at specific temperatures.

Table 1. Details of the chemicals, suppliers and purities of the components used in this study.

Chemical Name	Source	Mole % Purity	Certification	Analysis Method
MEG	Fisher Chemicals	99.9	Fisher Chemicals	GC
TEG	Fisher Chemicals	99.9	Fisher Chemicals	GC
Deionised Water	Pure Lab Elga 2	99	NA	NA
Methane	BOC	99.995	BOC Certified	GC

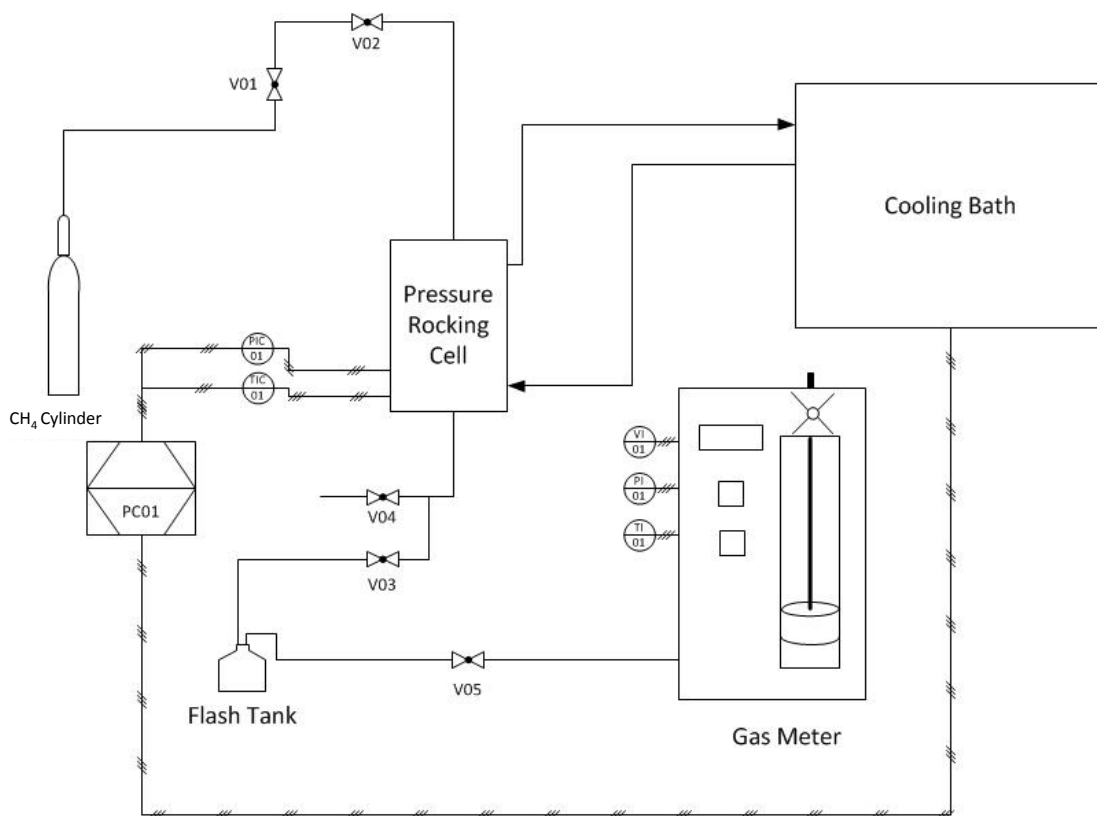


Figure 1 showing the rocking cell setup used to measure the solubility of Methane in glycol/glycol solutions PI01: Gas Meter Pressure Indicator; PIC01: Equilibrium Cell Pressure Indicator/logger; PC01: Computer Controller/Logger; TI01: Gas Meter Temperature Indicator; TIC01: Equilibrium Cell Temperature Indicator Controller; V01: CH₄ Cylinder Control Valve; V02: Equilibrium Cell Injection Valve; V03: Equilibrium Cell Drain Valve; V04: Equilibrium Cell Drain Valve (Backup); V05: Gas Meter Inlet Valve; VI01: Gas Meter Volume Indicator.

For the vapour phase, the experimental set-up used to determine the vapour phase concentration is comprised of an equilibrium cell, cryostat (for low temperature $T < 70^{\circ}\text{C}$), rocking/pivot mechanism, and temperature/pressure recording equipment controlled by a PC (Figure 2). The equilibrium cell is a piston-type variable volume (maximum effective volume of 300 ml) titanium cylindrical pressure vessel with mixing ball, mounted on a horizontal pivot with associated stand for pneumatic controlled rocking through 180 degrees. Rocking of the cell, and the subsequent movement of the mixing ball within it, ensures adequate mixing of the cell fluids. The rig has a working temperature range of -90 to 180°C , with a maximum operating pressure of 700 bar. The temperature is measured and monitored by means of a PRT (Platinum Resistance Thermometer) located within the cooling jacket of the cell. The cell temperature can be measured with an accuracy of $\pm 0.05^{\circ}\text{C}$. A Quartzdyne pressure transducer with an accuracy of ± 0.05 bar is used to monitor pressure. Temperature and pressure are monitored

and recorded by the PC through an RS 232 serial port. The cryostat can be monitored and controlled via an interface connected to a serial port on the computer.

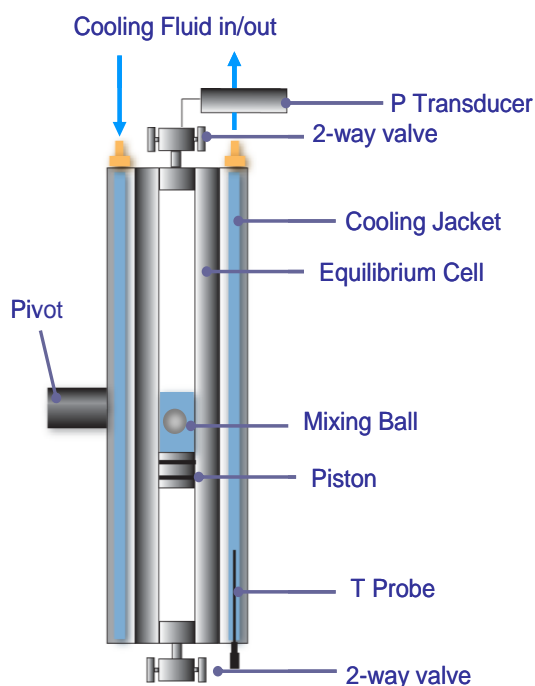


Figure 2. Schematic illustration of the equilibrium cell

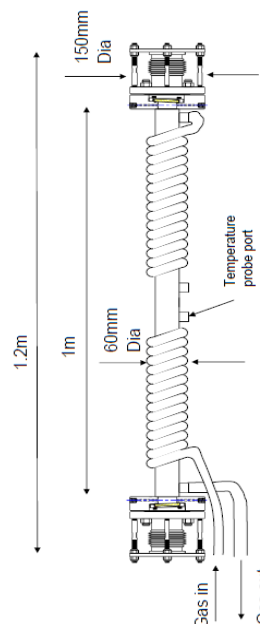


Figure 3. Schematic of the TDLAS set-up

For glycols determination an appropriate volume of the equilibrated gas is bled from the outlet of the cell at a controlled, steady flow-rate, passing through an adsorption tube with the desorbed gas collected in a volume-calibrated gasometer.). (NB: all sampling is conducted in an air-conditioned laboratory).

Sample volume requirement is determined by the expected equilibrated vapour concentration, whilst taking account of solute breakthrough volume for the adsorption tube deployed. The glycols' calibration mixtures are diluted in high purity methanol, and are introduced by GC syringe into the thermal desorption tube mounted in a commercially supplied Calibration Solution Loading Rig (CSLR), available from the manufacturer of the Thermal Desorption Analyser(TDA).

Sample collection tubes are then analysed in a 2-step procedure. First, the adsorbed glycols are thermally desorbed into a cooled trap in the form of a narrow, adsorption tube which condenses and refocuses the solutes. Secondly, the trap is rapidly heated, and simultaneously back-flushed from the TDA to an Agilent HP5890 gas chromatograph via a heated, insulated fused silica

capillary transfer line.. For water content determination, the outlet from the cell is connected to the gas inlet of a Tuneable Diode Laser Absorption Spectroscopy, TDLAS (Yokogawa) set-up. TDLAS is a spectroscopic technique that utilizes a diode laser as its light source. It works according to the fundamental principle of Beer's law. The principle involves concentrating near infrared light at a harmonic wavelength of the measured component (e.g., water). The molecules of the desired compound will absorb energy from the light and vibrate at very specific frequencies. The resultant loss of energy from the near infrared beam can be measured with a simple detector, and using the Beer Lambert law the concentration of the molecules in the media can be determined. More details on the experimental setup and the determination of water can be found in [5,6]

THERMODYNAMIC MODELLING

A full description of the original thermodynamic approach used to model the phase equilibria of methane with MEG,TEG or MEG/TEG solutions can be found elsewhere [2,7,8]. In summary the thermodynamic model is based on the uniformity of fugacity of each component throughout all the phases. The CPA-SRK72 (Cubic Plus Association – Soave-Redlich-Kwong) Equation of State (EoS) was used throughout this work to determine the component fugacity in all fluid phases. CPA parameters for water, MEG and TEG were taken from Kontogeorgis et al [9] and Derawi et al. [10], respectively. Critical properties of methane were taken from Poling et al [11].

RESULTS AND DISCUSSIONS

Gas Solubility

The solubility of methane in pure water at low temperatures has already been the subject of a study and many other authors have investigated this system at various conditions. Solubilities of methane in pure monethylene glycol (MEG) have also been reported in the literature: *Jou et al.* in 1994 [12], *Abdi et al.* in 2007 [13], *Folas et al.* [14] and by *Wang et al.* [15] in 2003. Solubilities of methane in pure triethylene glycol have also been reported in the literature. *Jou et al.* [16] have measured the solubility of methane in TEG over a wide range of temperature (25 to 125°C). *Wilson* [17] have also measured the solubility in TEG at low temperature. The new solubility data in pure glycols are plotted in Figure 4 with model predictions and literature data. As seen in the Figure, the new data agree well with the available literature data, and the

tuned model can reproduce the solubility of methane in glycols. It is worth noting that methane is far more soluble in glycols compared to water, i.e. 5.5 times more in MEG and about 21 times more in TEG (at 25°C and 100 bar).

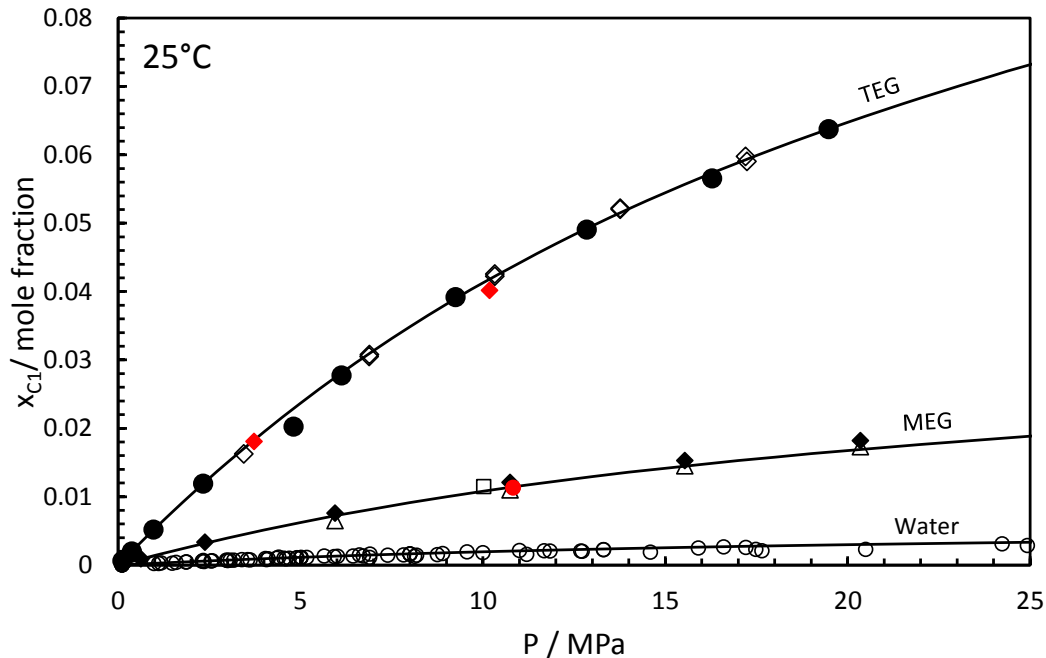


Figure 4 Experimental and predicted methane solubility in water, MEG and TEG at 25°C. Lines: CPA-SRK72 predictions; \circ , literature data methane solubility in water; \bullet , methane solubility in MEG this work; \blacklozenge , methane solubility in TEG this work; \blacklozenge , methane solubility in MEG [12]; \blacktriangle , methane solubility in MEG [13]; \square , methane solubility in MEG [14]; \bullet , methane solubility in TEG [16]; \blacklozenge , methane solubility in TEG [17].

Solubility data in aqueous solutions containing MEG have scarcely been investigated and have been only reported by Wang *et al.* [15] in 2003. New solubility measurements of methane in five different aqueous solution containing MEG (50, 80, 90 wt%) have been generated here at low and ambient temperatures. Some of the experimental data are shown in Figures 5 and 6.

As seen in Figure 5 the addition of 10 and 50 wt% resulted in a 36% and 76% average drop in the solubility of methane in MEG over the range. It can also be seen that the model tuned on binary data (Methane - MEG; Methane - Water and Water - MEG) failed to predict correctly the solubility of methane in the solutions, although the trend with pressure is correctly represented. The only data from the literature data available from comparison are the data from Wang *et al.* [15] at 80wt% MEG. Our data are in relatively good agreement with their (same order), however they do not show the same temperature dependency (Figure 6).

Similar observations can be made for the solubility of methane in TEG (Figure 7): 1. Addition of water greatly reduce the solubility (40, 61, 80 and 90% reduction in solubility in the 95, 90,

80 and 50wt% TEG solutions, respectively), 2. The model failed to correctly predict the solubility in the ternary systems.

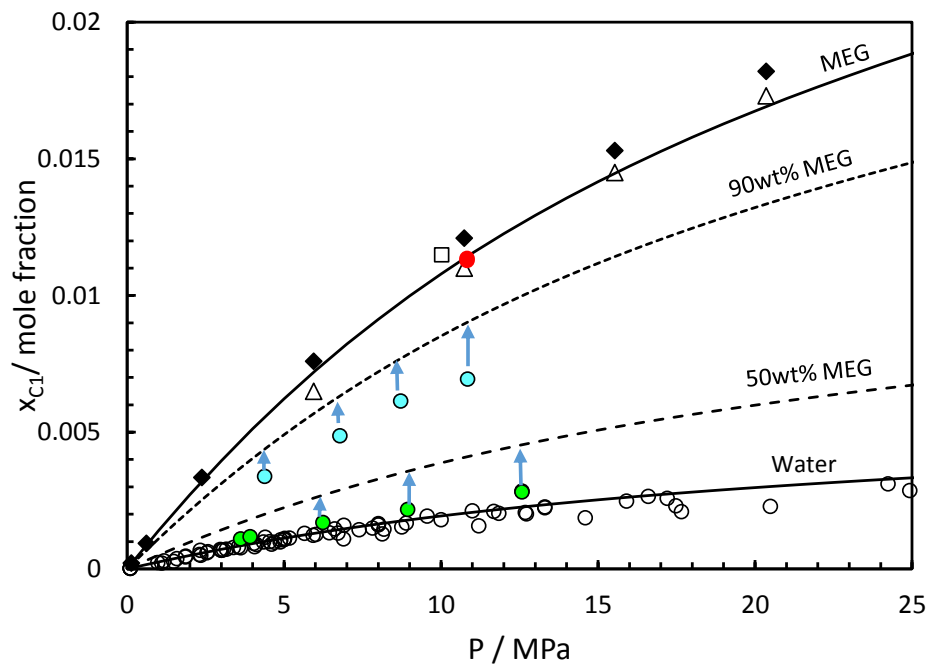


Figure 5 Experimental and predicted methane solubility in water, MEG and MEG aqueous solutions at 25°C. Lines: CPA-SRK72 predictions; \circ , literature data methane solubility in water; \bullet , methane solubility in MEG this work; \blacklozenge methane solubility in MEG [12]; \triangle methane solubility in MEG [13]; \square methane solubility in MEG [14]; \bullet , methane solubility in 90 wt% MEG solution, this work; \bullet , methane solubility in 50wt% MEG solution, this work.

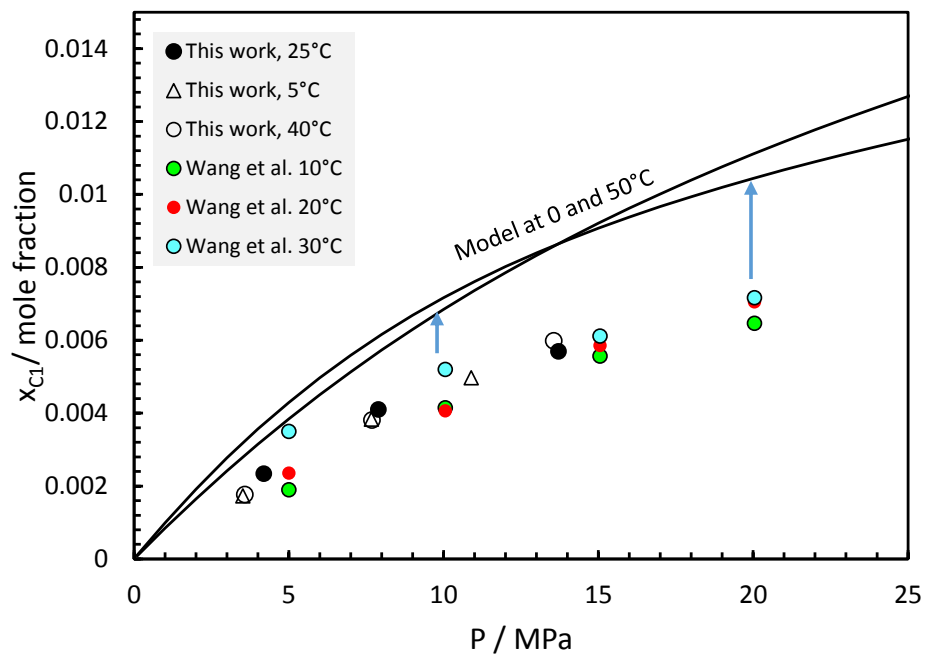


Figure 6 Experimental and predicted methane solubility in 80wt% MEG aqueous solutions at 5, 10, 20, 30 and 40°C. Lines: CPA-SRK72 predictions; \circ , \triangle , this work; \bullet , \bullet , \bullet , data from Wang et al. [15]

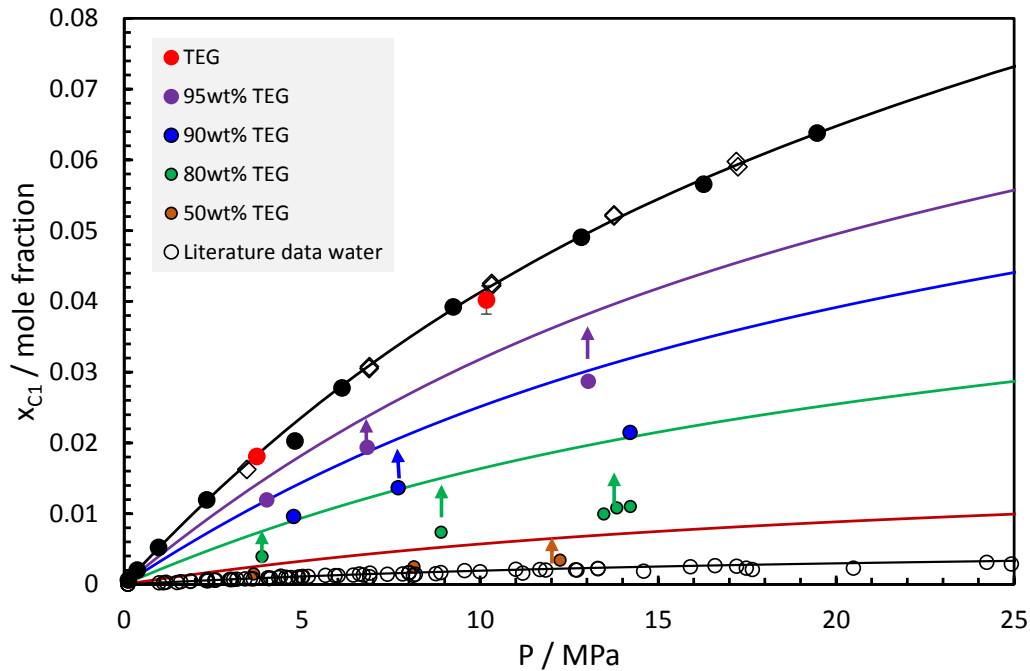


Figure 7 Methane solubility in TEG, water and TEG aqueous solutions at 25°C (lines predictions using CPA-SRK72 tuned on binary systems, i.e. methane – water, methane – TEG and TEG – water).

Glycol Partitioning

Few experimental data are available on the solubility of glycols in pressurized gases in equilibrium with pure glycols and to our knowledge, none are available for glycol solutions. MEG solubility in methane have been reported by Miguens et al. [18] and Folas et al. [14] between 0 to about 40°C and pressure up to 150 and 200 bar, respectively. Our new experimental data are plotted in Figure 8 (10°C) and Figure 9 (20°C) along with the model predictions and the above mentioned literature data. As seen in Figures 8 and 9., there is disagreement between the data set of Miguens et al. [18] and Folas et al. [14] (i.e. the data of Folas et al. [14] at 5°C are higher or of the same order than the data of Miguens et al. [18]). Our new data are in relatively good agreement with the data reported by Miguens et al. [18]. It can also be seen that the model tuned on solubility data can predict the MEG content accurately up to 100 bar but failed at higher pressure. Limited TEG solubility are available in the literature as seen in Figures 10 and 11, mainly due to the extremely low concentration of TEG in methane and the difficulty associated with measuring these traces. Extremely high scatter and disagreement are observed between these datasets. Our new experimental are also not in agreement with any of the available datasets, however they are close to the model predictions. Further experimental work is required to have a better understanding of the TEG behaviour.

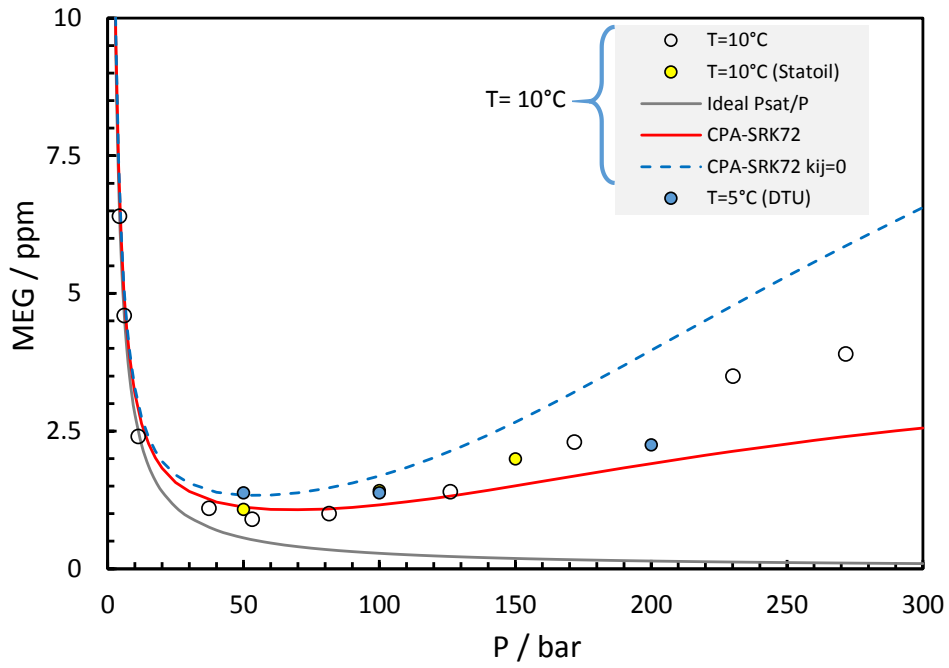


Figure 8 MEG solubility in Methane at 10°C and 5°C (lines predictions using CPA-SRK72 tuned on methane solubility data in MEG). Comparison with data from Statoil [18] and DTU [14]. Good agreement observed with the data of Statoil.

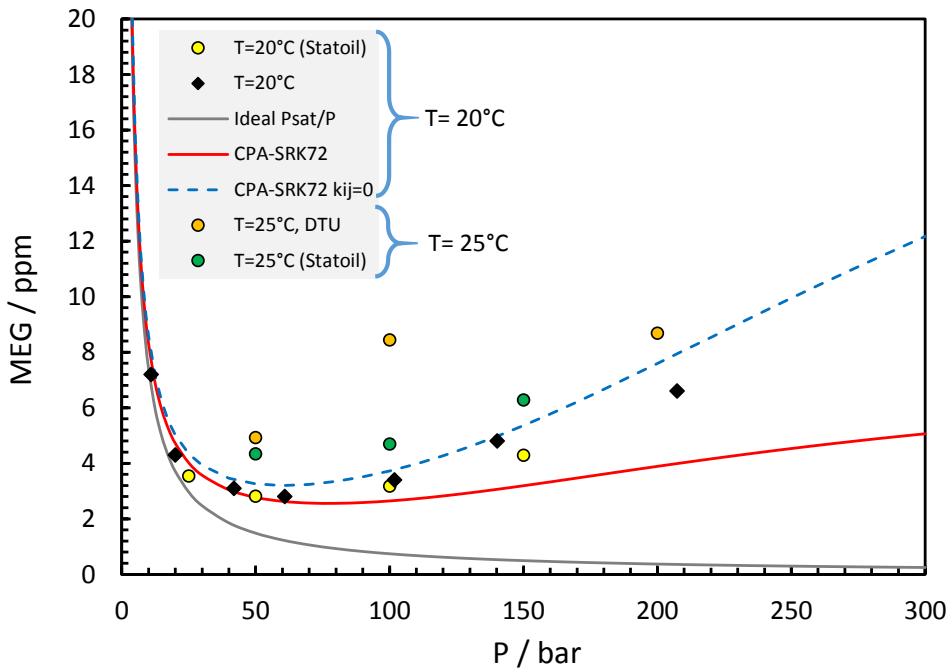


Figure 9 MEG solubility in Methane at 20°C and 25°C (lines predictions using CPA-SRK72 tuned on methane solubility data in MEG). Comparison with data from Statoil [18] and DTU [14]. Good agreement observed with the data of Statoil.

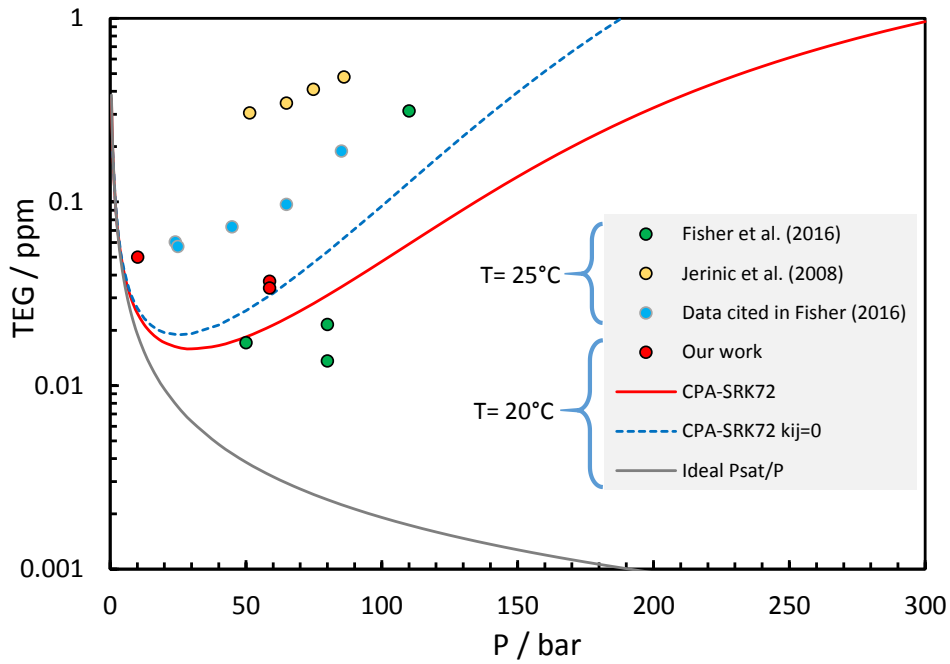


Figure 10 TEG solubility in Methane at 20°C and 25°C (lines predictions using CPA-SRK72/PCSAFT tuned on methane solubility data in TEG). Comparison with data from Fisher et al (2016) [19] and Jerinic et al. (2008) [20]

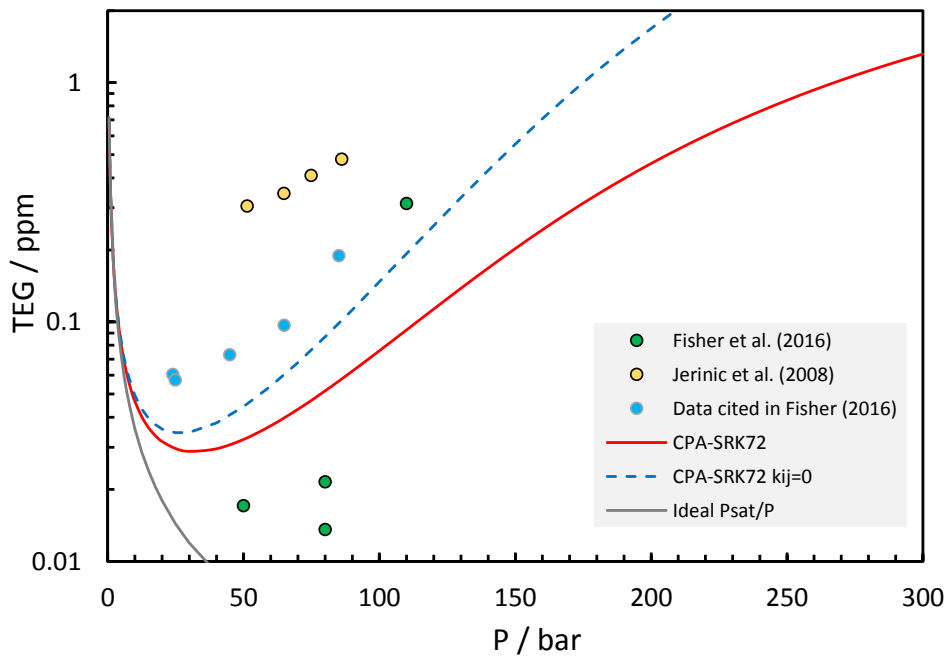


Figure 11 TEG solubility in Methane at 25°C (lines predictions using CPA-SRK72/PCSAFT tuned on methane solubility data in TEG). Comparison with data from Fisher et al (2016) [19] and Jerinic et al. (2008) [20]

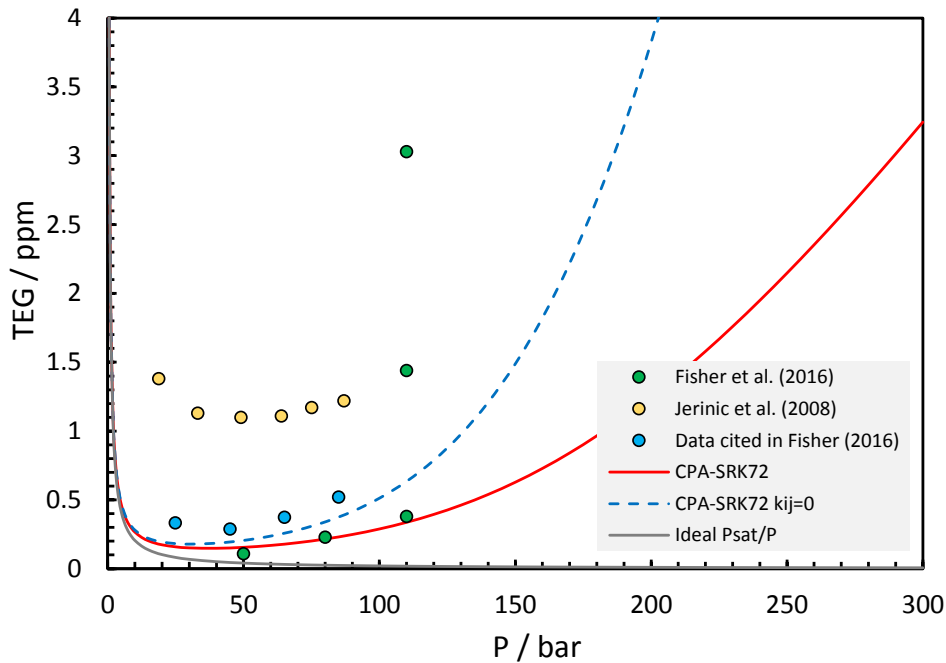


Figure 12 TEG solubility in Methane at 40°C (lines predictions using CPA-SRK72 tuned on methane solubility data in TEG). Comparison with data from Fisher et al (2016) and Jerinic et al. (2008) [20]

Water Content

Water content measurements for the multicomponent gas (in mole %: Nitrogen =7.0; Methane =84.13; ethane=4.67; propane=2.34; n-butane=0.93; n-pentane=0.93) in equilibrium with a 50 wt% MEG solution have been conducted for temperatures ranging from 0 to 10 °C at constant pressures (25, 50, 100 and 200 bar). As can be seen in Figure 13, the experimental conditions have been chosen to be outside the hydrate stability zone. Figure 14 presents the experimental data and the predictions of model and correlation developed in this work. The AAD with the model is 3%.

Water content measurements for the multicomponent gas in equilibrium with a 70 wt% MEG solution have also been conducted for temperatures ranging from -20 to 10 °C at constant pressures (25, 50, 100 and 200 bar). As can be seen in Figure 13, the experimental conditions have been chosen to be outside the 2 phase region of the system and outside the hydrate stability zone. Figure 15 presents the experimental data and the predictions of model and correlation developed in this work. The AAD with the model is 3%.

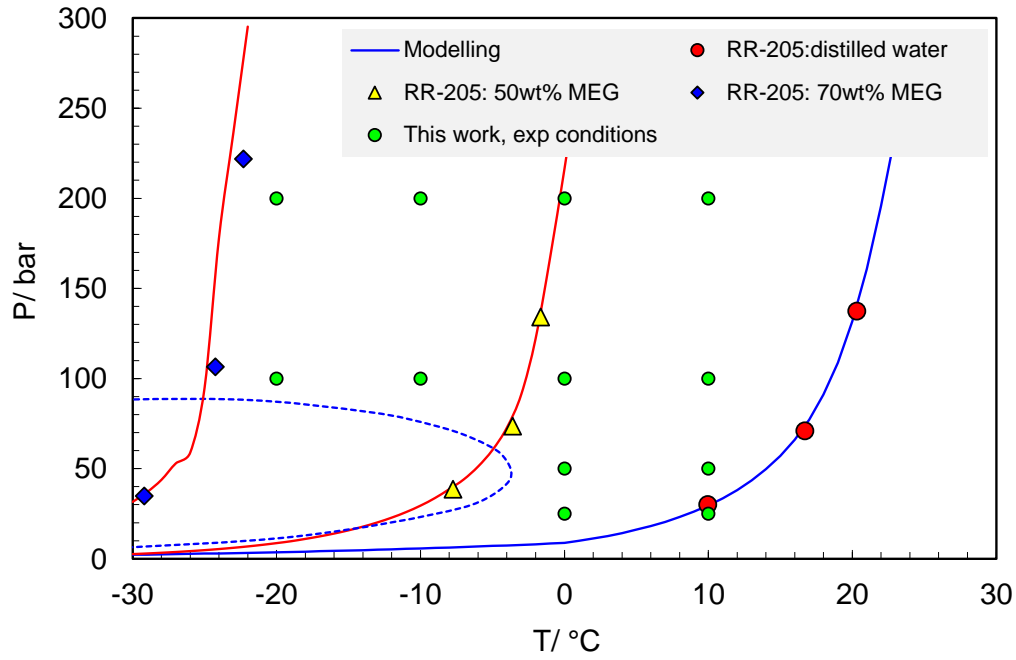


Figure 13 Experimental conditions and NG hydrate dissociation (sII) conditions in the presence of distilled water and MEG aqueous solutions (50 and 70 wt%) (Lines: CPA-SRK72) [21]

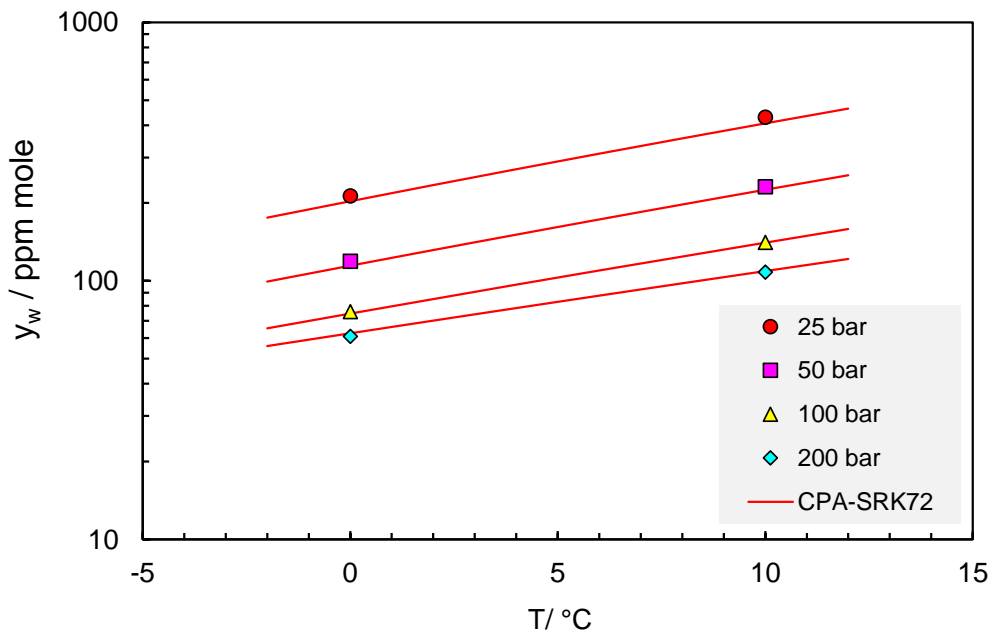


Figure 14 Experimental and predicted water content (ppm mole) of the natural gas in equilibrium with 50 wt% MEG aqueous solution at 25, 50, 100 and 200 bar (data from Chapoy et al. [22])

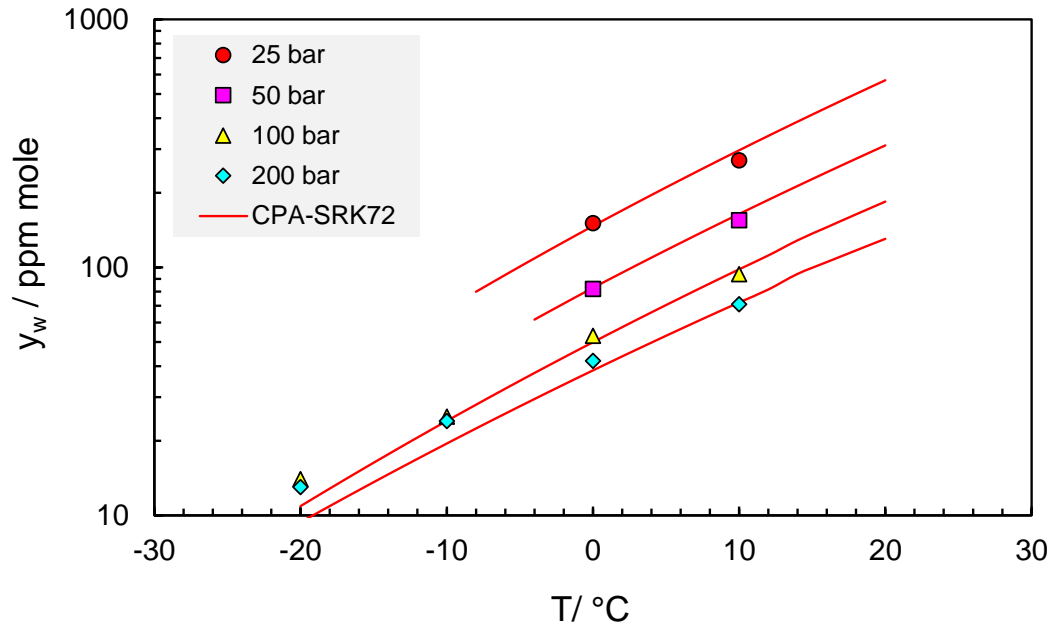


Figure 15 Experimental and predicted water content (ppm mole) of the natural gas in equilibrium with 70 wt% MEG aqueous solution at 25, 50, 100 and 200 bar (data from Chapoy et al. [22])

CONCLUSIONS

In this work the phase behaviour of methane – glycols and methane - glycols solutions have been investigated. From this work, the following can be concluded

- (i) The solubility of methane in MEG or TEG solution decreases significantly with the addition of water.
- (ii) For glycol solutions, the CPA-SRK72 demonstrated large deviation from the experimental results. Thus it may be concluded that CPA-SRK72 and other classical based EoS are not suitable for predicting accurately the phase behaviour of glycols and further development is required.
- (iii) MEG solubility can be predicted accurately up to 100 bar, however the model fails at higher pressure.
- (iv) Further work is required to estimate the TEG content in methane and validate model predictions. High discrepancies are observed between the available datasets.
- (v) Water contents are correctly predicted in a wide range conditions (temperature, pressure and MEG concentrations)

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