GLYCOLS IN NATURAL GAS – EXPERIMENTS, MODELLING AND TRACKING

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ABSTRACT

Glycols are important chemicals used in oil and gas production. Glycols are typically used for hydrate control and dehydration of natural gas. Glycols are low-volatility components, with low solubility in both gas and oil. However, operational experience shows that loss of glycols can give unwanted effects in downstream transport pipelines and process equipment. Few experimental data sets are published for glycol solubility in pressurized gases in the open literature. This paper presents experimental data for solubility of monoethylene glycol (MEG) in three gases (methane, CO_2, methane+ethane) measured in the temperature range from 0 to 25 °C and pressure range from 25 to 150 bar. The experimental data are compared to the CPA-EoS. The calculations are able to match the experimental data for MEG solubility in methane and methane+ethane with good accuracy at 50 bar. At higher pressure, the deviations between the model and the experimental data increases. MEG solubility in gaseous CO_2 was predicted with good accuracy for all measured points.

Keywords: Glycol, MEG, TEG, volatility, high pressure, methane, ethane, CO_2

NOMENCLATURE

AGRU	acid gas removal unit
CPA-EoS	cubic plus association equation of state
FID	flame ionisation detector
GC	gas chromatograph
LLE	liquid-liquid equilibrium
MEG	monoethylene glycol
MS	mass spectrometry
SLE	solid-liquid equilibrium
TD	thermal desorption
TD-GC	thermal desorption gas chromatography
TEG	triethylene glycol
VLE	vapour-liquid equilibrium
VLLE	vapour-liquid-liquid equilibrium
wt%	weight percent

INTRODUCTION

Use of glycols like monoethylene glycol (MEG) and triethylene glycol (TEG) is of high importance in modern oil and gas production. TEG is a common chemical used to dehydrate natural gas to pipeline quality specifications, while MEG is typically used to prevent hydrates formation during transport of reservoir fluids at low temperature. Even though the volatility of MEG and TEG in gas is low – traces of glycols will follow the export gas.

In this paper the importance of accurate knowledge of glycol loss to the gas phase is highlighted, and new experimental data for physical solubility of MEG in three gases (methane, CO_2, methane+ethane) is presented.

The results from the experiments are compared to a thermodynamic model based on the cubic plus association equation of state (CPA-EoS). This paper builds on a previous paper presented at IGRC 2008 [1] where effect of glycols on dew points of natural gas was discussed.

Glycol carry over to downstream processes can affect the performance of these processes. For example, it is important to know the glycol dew point of the natural gas at the acid gas removal unit (AGRU) inlet in order to determine the absolute glycol ingress to the amine units. Major quantities of the incoming glycols will accumulate in the amine units up to significant concentrations (> 15 wt%), since glycols are heavy boiling components and do not easily leave the system. They have a negative impact on the acid gas capture capacity and on the absorption kinetics and thus may limit the treatment capacity of a natural gas conditioning plant [2]. As well, glycols can reduce the capacity of adsorbents used in downstream processing [1].

In some gas sales contracts there are gas quality specifications setting limits for glycol content of the natural gas. Examples of such specifications can be "no free liquids" or less than 1 litre glycol/MSm^3 gas.

METHODOLOGY

Literature review
Glycols are low-volatility components, and experimental measurement of solubility in gas is challenging.

Few experimental data have been presented for the solubility of MEG and TEG in natural gas. Only two datasets have been published in the open literature presenting data for MEG and TEG in gaseous methane. The solubility of MEG in methane (and methane solubility in liquid MEG) was published by Folas [3] and the solubility of TEG in methane has been reported by Jerinic [4].

Experimental equipment and methods
The experimental equipment used in this work is a setup where high pressure gas is saturated with a liquid, before the temperature is reduced to allow for excess liquid to condense. The temperature is increased and the pressure is then reduced, and samples are taken in a low pressure sampling system. A schematic drawing of the rig is included in Figure 1, and a detailed description of the equipment is presented by Løkken [1].

Glycols are adsorbed on thermal desorption (TD) tubes, and the total volume of gas is measured by an analogue gas meter.
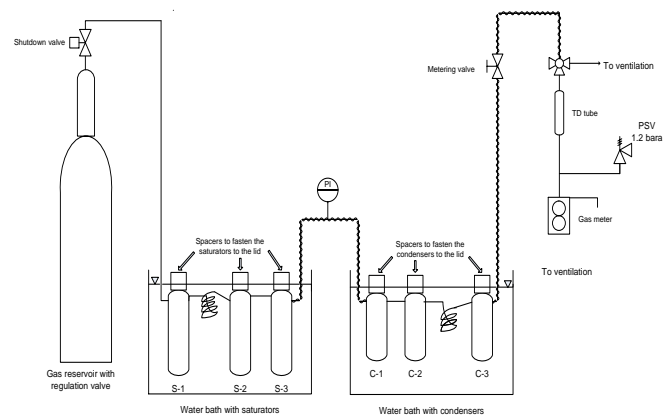

Figure 1: Schematic drawing of the rig.

The analysis of the samples taken from the experimental rig were analysed by a thermal desorption gas chromatography (TD-GC) technique. The samples were injected from the TD tubes, and were analysed by a gas chromatograph (GC). Two different instrumentations have been used, one where the GC is connected to a flame ionisation detector, FID, and one that has a mass spectrometry, MS, detector. The TD-tubes used are from Perkin Elmer and are coated with Tenax TA.

Thermodynamic modelling
In the modelling part of this work, an equation of state to predict the glycol content of gases in equilibrium has been used. The equation of state chosen is the CPA-EoS (Cubic-Plus-Association equation of state) [5] [6].

This model adequately describes LLE or VLLE of water and hydrocarbon systems [7] including also the solubility of hydrocarbons in the aqueous phase, LLE of glycol and hydrocarbon systems [8], VLE and SLE of water and glycol systems [3][10], VLE and SLE of alcohol and water systems [10], and mixtures with methanol or glycol as hydrate inhibitor [6] [11]. For non-associating compounds the model simply reduces to the classical SRK-EoS.

RESULTS & DISCUSSION

The experimental results are shown in Figure 2 (methane - MEG), Figure 3 (CO_2 - MEG) and Figure 4 (methane+ethane - MEG).

The solubility of MEG in methane has been predicted using the CPA-EoS with model parameters from [3] and has been included in Figure 2 for comparison.
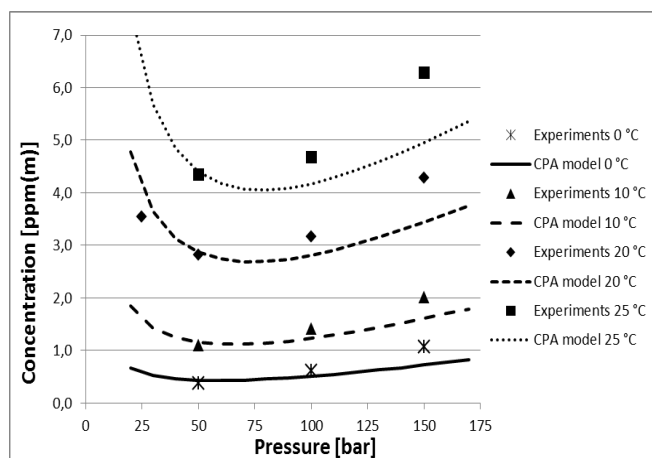

Figure 2: Results for the solubility of MEG in methane (ppm mole). Calculations using the CPA model have been included for comparison, and to make it easier to read the results at different temperatures.

The experimental results follow the trends expected based on theory and modelled values. The solubility increases for increasing temperature and pressure in the region between 50 and 150 bar, as seen in Figure 2. The experiments show that the solubility at 25 bar is higher than for 50 bar at 20 °C. This is also in

accordance with the theory and modelled values, as the solubility is expected to increase at low pressures after passing through a low point.

The calculations using the CPA-EoS are able to match the experimental data of MEG in methane with good accuracy at 50 bar. At higher pressure, the deviations between the model and the experimental data increases.

Experiments of MEG in carbon dioxide were done at temperatures of 0 and 20 °C from 10 to 50 bar. The solubility of monoethylene glycol in carbon dioxide has been calculated using the CPA-EoS. The results from the calculations have been included in Figure 3 for comparison with the experimental data.
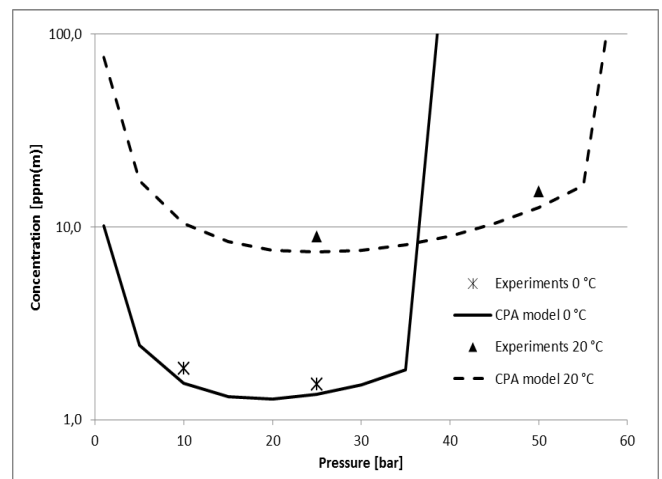

Figure 3: Results for the solubility of MEG in carbon dioxide (ppm mole). Calculations using the CPA model have been included for comparison, and to make it easier to read the results at the different temperatures.

The sudden increase in concentration observed is due to phase transition from gaseous to liquid CO_2.

The solubility of monoethylene glycol in 85 mol% methane and 15 mol% ethane has been calculated using CPA-EoS.

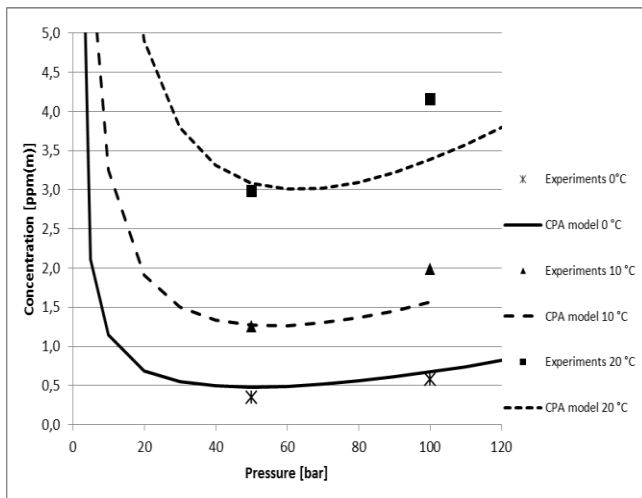A graphical representation of the results is shown in Figure 4.

Figure 4: Results for the solubility of MEG in 85 mol% methane and 15 mol% ethane (ppm mole). Calculations using the CPA model have been included for comparison, and to make it easier to read the results at the different temperatures.

As for the experiments of MEG solubility in pure methane, there is a good match to experimental data at 50 bar, but deviations start to increase at higher pressures.

Based on the experimental data and model presented in this paper, a case study has been to track MEG and TEG in downstream process units and transport system. The results from this case study illustrate the minimum amount of glycols that needs to be handled by downstream process equipment, and the importance of limiting glycol entrainment to downstream processes and transportation systems.

CONCLUSION

MEG solubility in methane, CO_2 and methane+ethane was experimental measured in dynamic saturating-condensing apparatus. The MEG was adsorbed on TD tubes and analysed by GC.

High accuracy is expected in the experiments (+/-10%). Predictions with the CPA-EoS were compared to the new experimental data in the temperature range 0 – 25 °C and pressure range 25 – 150 bar. The model matches the

experimental data with good accuracy at 50 bar. At higher pressures, the deviations between the model and the experimental data increases. Monoethylene glycol solubility in gaseous CO_2 was predicted with good accuracy for all measured points.

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