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# New association schemes for mono-ethylene glycol: Cubic-Plus-Association parameterization and uncertainty analysis

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ABSTRACT

Accurate thermodynamic predictions for systems containing glycols are essential for the design and commissioning of novel subsea natural gas dehydration units. Previously it has been shown that the Cubic-Plus-Association (CPA) equation of state can be used to model VLE, SLE and LLE for mixtures of interest to this application. Recent developments for association schemes have shown that the use of a binary association site provided improved modelling of 1-alkanols. In this work, we implement the binary association site for mono-ethylene glycol (MEG) by proposing three new association schemes (3C, 4E & 4F). New parameter sets have been regressed and uncertainty analysis, using the bootstrap methodology, was performed to obtain 95% confidence intervals for each parameter. An improved parameter set for the literature 4C scheme was also determined.

The four association schemes were tested against eight data types, with single parameter sensitivity analysis showing that new parameter sets are near optimal. The 3C scheme provides the best results for pure component properties and the liquid phase of MEG-$H_2O$, while new 4C parameters provide the best results for the MEG-$H_2O$ (vapour phase) and MEG-$nC_7$ LLE. For the limited ternary (MEG-$H_2O$-$CH_4$) data and MEG-$nC_6$ LLE, the best results are achieved using the 4F scheme. Ternary modelling performance was further improved by using binary interaction parameters fitted to binary vapour phase data.

While each of the new parameter sets provided an improvement over the literature parameters, it was found that no specific scheme was universally the best option. Given the uncertainty ranges and inconsistency between literature data, additional experimental data are required.

Despite the lack of sufficient data, the value of the bootstrap method has been highlighted, both for finding improved parameter sets and transferring uncertainty from experimental data through to thermodynamic and process models.

## 1. Introduction

The presence of water in natural gas and fuel gas pipelines presents a significant risk to continuous operability. Gas hydrate formation can cause pipelines to be completely blocked, while the combination of condensed water with carbon dioxide and hydrogen leads to corrosion [1]. Gas dehydration through absorption into tri-ethylene glycol (TEG) has become the natural gas industry standard for solving this problem, while mono-ethylene glycol (MEG) and methanol are also considered for direct injection applications due to their flow properties [2] and advantageous cost [3]. Other processing options, such as adsorption, refrigeration, membrane permeation and supersonic processing are available, but have several disadvantages for upstream and offshore applications [4]. Adsorption is typically preferred for ultra-dehydration applications, but has higher capital costs and a larger plant footprint. Refrigeration requires significant pressure drops to generate sufficient cooling. Use of membranes for water removal has seen some commercial implementation, although economically significant amounts of methane are lost along with the water [5]. Supersonic separators [6] offer interesting advantages for offshore applications, but along with membrane separators [7], are still very much in development and are unlikely to see significant market penetration in the near future [4].

For absorption into liquid desiccants, TEG provides greater dew point depression capability, while direct injection with MEG

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provides sufficient dehydration and hydrate inhibition for flow assurance and operability. This is of particular interest in subsea networks, where essentially untreated gas is transported over long distances to central processing facilities. Occasionally di-ethylene glycol (DEG) or MEG/DEG mixtures are used to negate the higher relative volatility of MEG (which leads to losses to the gas phase), but these types of installations are less common. Statoil is currently developing the Gas-2-Pipe™ process [8], which aims to produce on-specification export gas (or Sales Gas) at the seabed. The main specifications are the hydrocarbon dew point, water dew point and glycol content of the gas according to the GASSCO specifications [9], while the processing conditions between 50 and 150 bar, 5 °C (278 K) and glycol content >90 wt% are envisioned.

Proper design of dehydration and hydrate inhibition processes requires a combination of a high quality experimental data and thermodynamic models. The scarcity of data for systems of interest to this investigation has been highlighted in several sources [3,10–13] and very often the available data are contradictory. Additionally, the gas phase quantification of glycols at operating temperatures and pressures is especially challenging as these compounds occur in the low ppm range, which is near the detection limits of gas chromatography [14].

The Cubic-Plus-Association (CPA) [15,16] equation of state (EoS) has been previously implemented for the thermodynamic modelling of gas-water-glycol and gas-condensate-water-glycol systems. CPA is a five-parameter equation of state which combines the repulsive and attractive terms of the Soave-Redlich-Kwong (SRK) [17] with the association term first proposed by Wertheim [18–21] and later implemented in an engineering form by Chapman et al. [22,23] into the Statistical Associating Fluid Theory (SAFT) equation(s) of state. The association term is used to account for intermolecular hydrogen-bonding using a site-specific scheme which must be defined for each molecule. Traditionally, alcohols have been described with the 2B scheme (1 positive and 1 negative site), while glycols and water have been represented with the 4C scheme (2 positive and 2 negative sites). For almost twenty years, there were relatively few developments with respect to association schemes. However in 2009 [24] and 2011 [25], new association schemes were proposed for glycols (6D) and 1-alcohols (2C). The 2C scheme of de Villiers et al. [25] is especially interesting as it makes use of the binary site (universal bonder), which had previously only been applied for acid dimerization (1A scheme).

More recently the need has arisen for robust quantification of the uncertainty and/or sensitivity analysis of both experimental data and thermodynamic models as applied in process design. As Mathias [26] points out: *"Several studies have illustrated the effects of uncertainty in the physical-property models on process design, however these publications do not provide an effective way to quantify the propagation of the property uncertainty into design variability."* Despite this need and the obvious advantages of understanding modelling uncertainty, Mathias notes that uncertainty analysis has seen limited implementation in industry. Mathias proposed a method for incorporating property uncertainty as a perturbation to the activity coefficient, using an adjustable parameter to give the magnitude of the perturbation. Asprion et al. [27] applied this concept to equations of state by perturbation of the fugacity coefficient.

Another approach was taken by Bjørner et al. [28], who applied a statistical method - called bootstrapping - to determine the confidence intervals for the parameterization of $CO_2$ within different variations of CPA. While this method appears more complex, the implementation is relatively straight-forward and has the added advantage of using experimental data (rather than adjustable parameters) to determine the confidence intervals or uncertainty.

Within this work, we build on the work of de Villiers et al. [25] by proposing new association schemes for glycols which incorporate the binary association site. Necessarily, new parameter sets must be regressed, for which the bootstrapping technique is applied for determining parameter confidence intervals. A thorough evaluation of the literature data is required, which will focus on light hydrocarbon, water and glycol mixtures – as the application of this work is natural gas dehydration. Higher hydrocarbons will however not be ignored, as their present risk to both operability within the dehydration process and asset management of downstream transport networks [14,29].

## 2. Literature review

### 2.1. Literature data of interest to glycol-based dehydration studies

Both pure component ($P_{SAT}$ and $\rho$) and mixture data (binary LLE) have been identified as critical for the evaluation of model parameter sets [30]. As this work is geared towards natural gas dehydration applications, good modelling of glycol-water and natural gas-glycol-water systems (necessary for the design of the absorber and regeneration processes) are focussed on.

In terms of determining process feasibility, the measurement of water and glycol in the vapour phase are essential as these are critical specifications for the final gas product. Overprediction could lead to the rejection of perfectly acceptable process configurations, while underprediction will result in off-spec production and/or downstream asset integrity issues. The lack of experimental data (especially for MEG in the vapour phase) is due to the difficulty of measuring low levels of MEG using standard gas chromatography.

Gas solubility data are very important for the determination of hydrocarbon carryover into the regeneration processes and the subsequent emissions there [31]. For this purpose, other studies have also investigated mixtures including aromatic (BTEX) compounds [10,32].

#### 2.1.1. Pure component data

For many studies, the DIPPR correlations (which are fitted to multiple experimental data) have been used to generate pseudo-experimental data at equally spaced intervals for reduced temperature ($T_R$) ranges of approximately 0.4–0.9. Fig. 1 highlights the degree to which the correlations are extrapolated beyond the experimental data (for MEG), with 95% of the vapour pressure and density points below $T_R = 0.67$ and 0.58 respectively. For reference, the proposed subsea dehydration would occur between 273 and 303 K (depending on the location of the installation) (approximately $0.38 < T_R < 0.42$), while regeneration typically occurs at higher temperatures (up to ~ 473 K which is $T_R = 0.66$). Very few data are available around $T_R = 0.4$ – especially for glycol vapour pressure, as the experimental values become very low and exceedingly difficult to quantify accurately.

Recent work by Crespo et al. [33] provides high pressure density data up to 950 bar and ~363 K for several glycols including MEG and TEG.

#### 2.1.2. Binary data

While there are several pure component data available for vapour pressure and density (if not in the desired ranges always), there are serious concerns with respect to binary, ternary and multicomponent data. For MEG-$CH_4$, only Folas et al. [14] quantify both phases. Only for three data points were measured however, making thermodynamic consistency tests impractical. Furthermore, several sources from the open literature have measured $CH_4$ solubility in MEG [14,34–38], but only three (Folas et al. [14], Berså̊s [39] and Miguens et al. [40]) present data for glycol in the vapour