Accounting for cross association in non-self-associating species using a physically consistent SAFT-VR Mie approach

This work presents a formalised, physically consistent approach to account for cross association in the SAFT framework. The focus of the approach was to account for solvation of non-self-associating components, using members of the ketone and ether functional groups as model components. Physical consistency is captured by only considering a single negative site in these components, with the association mechanisms termed the “N scheme” as a result. An accurate polar parameter set is a prerequisite for the approach, where polar and dispersion interactions are already accounted for in pure component properties and those of mixtures where solvation is absent. Using SAFT-VR Mie-GV as the example framework, the approach considers the discretisation of the two association parameters, and it applies the resulting matrix of parameter sets to mixture VLE data for the ketone or ether with alcohols in the C₂ to C₄ range. Analysis of the resulting AAD contour plots demonstrate that the use of average solvation parameters for each functional groups are appropriate, rather than component-specific parameters, and they offer excellent pure predictions for alcohol mixtures and good predictions for aqueous mixtures. As a final test, the approach was applied to chloroform, considering a single positive site and using the proposed parameterisation method. The resulting “P scheme” for chloroform, in conjunction with the N scheme for acetone, yields excellent predictions for the quintessential chloroform/acetone mixture and emphasises the suitability and predictive strength of the approach.
Multicomponent Vapor–Liquid Equilibrium Measurement and Modeling of Ethylene Glycol, Water, and Natural Gas Mixtures at 6 and 12.5 MPa

High pressure subsea natural gas dehydration (NGD) units using ethylene glycol (MEG) absorption have been proposed. To expand the experimental database and assist design qualification, new vapor–liquid equilibrium (VLE) experimental data have been measured for a 20-component glycol–water–natural gas mixture at $T = (288–323) \text{ K}$, $p = (6.0, 12.5) \text{ MPa}$, and $w_{\text{MEG, feed}} = (90, >99.8) \%$. MEG, H$_2$O, CO$_2$, N$_2$, and alkane (methane to n- and i-pentane) phase distributions have been quantified. Experimental uncertainty ranges from ±2–42%, with the greatest uncertainty for the quantification of trace components. Experimental results are modeled using the Cubic-Plus-Association (CPA) equation of state. Overpredictions (–9%) are observed for the water content of the vapor phase. CO$_2$ is shown to have a large effect on $y_{\text{MEG}}$, leading to modeling deviations in the order of 65%. A relatively accurate prediction of the natural gas partition coefficients was observed for major components C$_1$–C$_3$ and CO$_2$, with modeling errors ranging from 5% for methane to 10% for CO$_2$. More significant deviations were observed for trace components, with the largest deviation of 73% N$_2$. The CPA model provides both satisfactory and conservative results suitable for use in NGD process designs. On the basis of this work, operation at subsea conditions would significantly improve dehydration capability.

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

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-H₂O, while new 4C parameters provide the best results for the MEG-H₂O (vapour phase) and MEG-
nC7 LLE. For the limited ternary (MEG-H₂O-CH₄) data and MEG-nC₆ 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.

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Ternary Vapor–Liquid Equilibrium Measurements and Modeling of Ethylene Glycol (1) + Water (2) + Methane (3) Systems at 6 and 12.5 MPa

Novel technologies in the field of subsea gasprocessing include the development of natural gas dehydration facilities, which may operate at high pressure due to their proximity to reservoirs. For the qualification and design of these processing units, ternary vapor−liquid equilibrium data are required to validate the thermodynamic models used in the design process. For this purpose, 16 new ternary data points were measured for ethylene glycol (1) + water (2) + methane (3) at 6.0 and 12.5 MPa with temperatures ranging from 288 to 323 K and glycol content above 90 wt %. Glycol in gas (y1), water in gas (y2), and methane solubility (x3) were measured with relative experimental uncertainties (ur(x) = u(x)/|x|) below 12%, depending on the type of data. The Cubic-Plus-Association (CPA) equation of state was used to model the data. Literature pure component and binary interaction parameters were used. It was found that the model provides a good qualitative description of the experimental data for y1 and y2, while a significant over-prediction occurs for x3. The modeling errors for CPA ranged between 5–40% average absolute relative deviation.

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Monomer fraction data of dilute alcohol/acetone systems measured with transmission Fourier transform infrared spectroscopy

New monomer fraction data (fraction of non-hydrogen bonded molecules) of dilute (x(solute) <0.016) C4 to C3 alcohol-in-acetone and dilute acetone-in-alcohol systems were collected via Fourier transform infrared (FTIR) spectroscopy. Monomer fraction data may be used to improve regression parameters within the Statistical Associating Fluid Theory (SAFT) modeling framework. For very dilute (x_{alcohol} <0.003) alcohol-in-acetone mixtures, it was found that 2-propanol had the highest monomer fractions and methanol had the lowest. As the alcohol mole fraction increased (x_{alcohol} > 0.003), methanol maintained the lowest monomer fraction (\(X_{mon,MeOH} = 0.01\) at \(x_{MeOH} = 0.0086\)), with ethanol, 1-propanol and 2-propanol approaching similar monomer fraction values, i.e., \(X_{mon,X-alcohol} \rightarrow 0.06\). For dilute acetone in alcohol, and especially for methanol and ethanol, there was a pronounced trend towards acetone monomer fractions of 1 at infinite dilution. The acetone monomer fractions decreased according to an exponential decay function to values of +/- 0.3 for acetone dissolved in methanol and +/- 0.1 for the other alcohols investigated. Acetone monomer fractions, therefore, tended to decrease as alcohol chain-length increased, showing that acetone could more easily penetrate the hydrogen bond network of the solvent when the solvent/solvent hydrogen bonds were weaker. For dilute acetone in 2-propanol, a previously unrecorded monomer peak was observed and quantified. (C) 2015 Elsevier B.V. All rights reserved.
Over the past 25 years, offshore gas processing operations have seen a proliferation in the development of subsea installations with complete subsea processing facilities soon to be a reality. Novel technologies – including subsea...
dehydration and compression units – are aimed at gas-dominated wells with the purpose of production and export directly from the seabed. Subsea production presents opportunities for improved efficiencies and increased profitability. To achieve the required dew point specification, water is absorbed from the gas stream through contact with a glycol such as ethylene glycol (MEG). The design and operation of these dehydration units require a thorough understanding of the phase equilibrium between the gas, water and glycol, at the process conditions observed in subsea installations. This understanding is achieved through a combination of accurate phase equilibrium data and thermodynamic models.

For this purpose we have performed phase equilibrium measurements for two systems: MEG + H₂O + CH₄ and MEG + H₂O + Natural Gas. Experimental temperatures range from 15 – 50 °C, with measurements at pressures of 60 and 125 bar. The experiments were performed in a purpose-built rig at Statoil’s Research and Development Center in Trondheim, Norway. Glycol-rich mixtures have been prepared (>90 wt% in the liquid phase) in order to replicate dehydration applications. Glycol content has been determined using adsorption tubes which are analysed in a GC-MS, while water content was measured using Karl Fischer titration. For the natural gas systems, component analysis for C₁-C₆, N₂ and CO₂ has been performed with the use of gas chromatography. The experimental uncertainty is shown to be ~10% depending on the type of measurement.

Thermodynamic modelling is done using the Cubic-Plus-Association (CPA) equation of state. The model provides a good qualitative description for the vapour phase content for MEG and H₂O, which are critical product specifications for dehydrated natural gas. For the description of MEG, we evaluate the performance of our new 4F association scheme against the literature 4C scheme. The use of uncertainty analysis in the parameterization of the models allows for the determination of operating ranges for process designs. This transference of uncertainty, from the data to the model and to the design, provides greater insight for the decision-maker regarding the process feasibility of a given design.

Degree of recognition: International

**Related external organisation**

**Institute of Chemical Process Fundamentals of the CAS**
Czech Republic

Activity: Talks and presentations › Conference presentations

**A new association scheme for mono-ethylene glycol within Cubic-Plus-Association equation of state**

Period: 19 May 2017
Francois Kruger (Guest lecturer)

Center for Energy Resources Engineering
Department of Chemical and Biochemical Engineering
CERE – Center for Energy Resources Engineering

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Francois Kruger (Recipient)
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