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.