Solid-Fluid Equilibrium Measurements of Benzene in Mixed Solvents and Hydrogen Sulfide in Methane

Wanying Wu[1, S], Mark Barwood[1], Peter Metaxas[1], Paul L. Stanwix[1], Brendan Graham[1] and Eric May[1, C]

[1]*Fluid Science and Resources, Department of Chemical Engineering, School of Engineering, University of Western Australia, Perth, Australia*
eric.may@uwa.edu.au

Unprocessed natural gas contains a wide range of impurities. Prior to liquefaction, the gas needs to be cleaned and dried by removing hydrocarbons, acid gas components, and water. Despite this, impurities at concentration as low as parts-per-million (ppm) can still freeze out and lead to blockages in cryogenic heat exchange equipment and pipelines, causing safety and economic problems. However, accurate prediction of solid-fluid equilibrium (SFE) conditions and the rate at which these solids form in LNG mixtures is challenging due to scarce high-resolution experimental data and a lack of high-accuracy engineering models.

To close the knowledge gaps present in people's understanding of SFE and solid formation kinetics, our group has recently published optical measurements of C_6H_6, H_2O, and CO_2 freeze-out from CH_4 at LNG-relevant conditions [1-3]. These results have been used to tune the impurity-methane binary interaction parameter for these compounds to improve the accuracy of SFE predictions from thermodynamic models. However, a real LNG mixture is a complex mix of fluids including C_2H_6 and N_2. As a result, measurements are now being continued for benzene freeze-out from mixed solvents (e.g., C_6H_6 in CH_4 + N_2, C_6H_6 in CH_4 + C_2H_6). Benzene (C_6H_6) is one of the most problematic hydrocarbon compounds as it can freeze out at relatively high temperature at ppm-level concentrations in CH_4. In addition to the measurements of C_6H_6 in mixed solvents, we are extending this work to other impurities commonly present in natural gas such as H_2S.

The SFE data situation for these mixtures is relatively poor; there are none available for the C_6H_6-CH_4-N_2 system and only scarce data for the C_6H_6-CH_4-C_2H_6 ternary and H_2S-CH_4 binary. To address this problem, this work will present high-resolution optical measurements of C_6H_6 solubility in CH_4 + N_2 and CH_4 + C_2H_6, and H_2S solubility in CH_4. These SFE and solid formation results are used to develop thermodynamic and kinetic models for these mixtures. Ultimately, this work can help LNG plant operators better characterise the process conditions under which C_6H_6 and H_2S may cause a freeze-out risk.

References

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