An Improved Approach to Cryogenic Solid Solubility Prediction via the Poynting Factor Approximation

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The presence of impurities (heavy hydrocarbons/sulfur compounds for liquefied natural gas; oxygen, nitrogen, argon, methane and ethane for liquefied hydrogen) can pose a significant challenge for industrial liquefaction processes due to the risk of solid formation as the fluid mixture is cooled. In severe cases, this "freeze-out" can lead to blockages which necessitate a plant shutdown and result in a substantial cost penalty (e.g., $30 million per missed cargo [1]). Accurate prediction of the solubility of trace levels of impurities is therefore key to ensuring reliable plant operation. Such modelling requires predictions of solid fugacities at high pressures and cryogenic temperatures, which in most software packages is provided by the so-called "classical" solid fugacity model. In this approach, basic properties of the pure substance at the triple point are used to estimate the solid fugacity, and binary interaction parameters are tuned to improve the solubility predictions of mixtures. This approach has the drawback that its predictions can become inaccurate at conditions far from those of the data used in tuning. An alternative, more fundamental method for solid fugacity computation would be beneficial.

In this work, we propose an improved approach to predicting the solubility of trace solid impurities in cryogenic fluids using solid fugacity estimations based on the Poynting factor approximation. Sublimation pressure and solid cell volume of 33 components have been fitted via polynomial correlations and, together with the pure fluid fugacity at saturation pressure, these may be used to determine the solid fugacity. Using a range of experimental solubility data, we compare the predictions of this model to the classical model, as well as to the Helmholtz solid equations of state which have previously been developed for benzene and carbon dioxide.

References

1. Baker, C.J., et al., *Rapid simulation of solid deposition in cryogenic heat exchangers to improve risk management in liquefied natural gas production.* Energy Fuels, 2018. **32**: p. 255.