

Modelling gas clathrate hydrates using SAFT-VR

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Gas clathrate hydrates are crystalline inclusion compounds in which a water host lattice encages small guest atoms or molecules. They are environmentally important as a potential means for CO₂ capture and also in terms of the vast oceanic reserves of methane hydrate, which represent both a potential source of fuel for the future and a potential threat in the event of methane escape to the atmosphere. They are important in the oil and gas industry because they form in and clog pipelines during oil and gas recovery.

Modelling the phase equilibria of hydrate systems is, in some respects, a solved problem; accurate calculation of the hydrate locus for many simple and mixture gas hydrates has been possible for decades. At the core of many modelling techniques is the statistical-thermodynamic treatment of van der Waals and Platteeuw [1], first published almost 50 years ago and generalised to mixtures by Parrish and Prausnitz [2] in the 1970s.

However, an important constituent part of the modelling is the thermodynamic treatment of the fluid phases, which requires the use of an equation of state (EOS). The accuracy of any prediction is thereby limited by the ability of the EOS to represent accurately the free energy of the fluid phases. In the case of simple systems involving only water and the guest gases, the water and gas phases can be treated independently; here traditional cubic EOSs provide for excellent prediction. However, in practice, systems may be more complicated, involving hydrate inhibitors such as methanol or glycol, and / or salt; in these cases the use of a traditional cubic EOS provides less-reliable predictions, requiring some adjustment to be made to the method, such as the use of an activity-coefficient model to treat the liquid phase.

The statistical associating fluid theory (SAFT) is specifically designed to treat associating systems such as those involving water and methanol. It provides excellent representations of the thermodynamics of the important hydrate-forming gases [3] and, moreover, has been shown to be effective in the treatment of electrolyte systems [4,5].

In this work we introduce SAFT-VR to a van der Waals and Platteeuw modelling framework, thereby providing a thermodynamically consistent platform on which to improve the reliability and predictive capability of hydrate modelling in industrially relevant systems. In particular, to describe the interaction between the water molecules forming the hydrate cages and the guest molecule, we use a square-well cell potential related to that used within the SAFT theory, thereby creating a direct link between the interaction of a guest molecule and water in the hydrate, and their interaction as fluids.

References:

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