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Multiple Hydrate Structure Formation in Natural Gas Systems: Experimental Measurements and Modelling

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While extensive experimental data and predictive modelling capabilities now exist with respect to incipient clathrate hydrate phase boundaries for single to multi-component natural gases, including complex systems involving liquid hydrocarbons, salts and thermodynamic inhibitors, phase behaviour within hydrate regions is far less well constrained, even though this is of great importance to both natural and industrial hydrate environments.

In many real-world situations, hydrate formation may take place far inside the phase boundary. Under such conditions, multiple stable/metastable clathrate phases may nucleate, grow, dissociate and/or undergo direct solid-solid transitions as systems tend to equilibrium.

In related works, it is described how such multiple structure formation processes are apparently closely linked to hydrate agglomeration / plugging tendency, natural slurry transportability, and LDHI (AA and KHI) performance. The same processes can likewise be expected in sediment-hosted gas hydrate systems, e.g. during gas production or CO₂ injection. For example, recent laboratory studies have shown clear evidence for multi-hydrate phase formation and solid-solid transitions during simulated flue gas sequestration in permafrost sediments.

Here, we present constant volume isochoric equilibrium PVT (pressure-volume-temperature) data for several natural gas systems that show the sequential formation of multiple hydrate phases/structures at equilibrium as subcooling / hydrate fraction increases. Depending on the initial PT conditions of hydrate growth, persistent structural hysteresis can also be observed, resulting in more than one (metastable?) equilibrium state. PVT data are supported by QCM (quartz crystal microbalance) studies that provide evidence for solid phases undergoing crystallographic / structural changes at higher subcoolings, including in single guest gas systems such as methane.

With the aim of better understanding the processes involved, an in-house thermodynamic model – which uses the CPA equation of state for fluid phases and the solid solution theory of van der Waals and Platteeuw for hydrate phases – has been used to predict observed behaviour, including the phase boundaries and fractions of structures present. Predictions agree well with experimental data, and support the sequential growth (as temperature is reduced) of a series of hydrate phases typically beginning with propane/butane stabilised (large cavity) s-II, followed by ethane stabilised (large cavity) s-II then s-I, before final methane-dominated s-I. At equilibrium, behaviour is ultimately driven by gas fractionation, although as noted, significant structural hysteresis and metastable phases can form depending on initial growth PT conditions, including a metastable s-II methane hydrate.

In addition to equilibrium predictions, boundaries for non-equilibrium incipient hydrate formation conditions are also predicted. These delineate the PT conditions where different hydrate structures can grow at subcooling even if they may not be the most thermodynamically stable phase, as observed in experimental studies. Such predictions are particularly important for flow assurance applications where hydrate growth may initiate at high subcoolings, e.g. in the case of KHI failure or following shut-in, cool-down and restart.