Surfactant Adsorption to Gas Hydrate Interfaces Quantified by Differential Scanning Calorimetry

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Gas hydrates are crystalline solids that can form and plug subsea oil and gas pipelines. With focus shifting from the complete prevention of hydrate to limiting the severity of hydrate formation, high-performance surfactants (i.e. anti-agglomerants) can be central to the strategy of preventing the formation of a hydrate plug. Currently, the performance of each anti-agglomerant and petroleum fluid pairing is validated qualitatively in a rocking cell, which does not capture the amount of surfactant required for adsorption at the hydrate-oil interface. In this study, a differential scanning calorimeter (DSC) method was developed to investigate methane hydrate formed at high pressure from a water-in-crude oil emulsion. A metastable crude oil emulsion was chosen for this study, for which the droplet size distribution was determined with low-field NMR and visual microscopy. Representative surfactants were added to the crude oil phase across a wide range of concentrations, including model chemicals for an industrial corrosion inhibitor and hydrate anti-agglomerant. The minimum concentrations of these surfactants required for adsorption were successfully identified using repeated hydrate formation and dissociation trials in the DSC, and compared to previously-reported estimates for hydrate systems. The results indicate that corrosion inhibitor chemistries are clearly active at the hydrate-oil interface and were able to stabilize the hydrate dispersion at concentrations above 0.001 wt% in oil. Without the addition of synthetic surfactants, increasing the brine salinity to 10 wt% fully stabilised the hydrate-in-oil dispersion without significantly affecting the water droplet emulsion stability. This suggests that brine salinity is a key parameter in tuning the performance of surfactants for hydrate-in-oil dispersions.