Corrosion inhibitor interaction at hydrate–oil interfaces from differential scanning calorimetry measurements

Zachary M. Aman*, Kristopher Pfeiffer, Sarah J. Vogt, Michael L. Johns, Eric F. May

Centre for Energy, School of Mechanical and Chemical Engineering, University of Western Australia, 35 Stirling Highway, Crawley 6009, WA, Australia

HIGHLIGHTS

- Hydrate-in-oil stability was quantified with differential scanning calorimetry.
- Method identified corrosion inhibitor adsorption to hydrate surface.
- Corrosion inhibitors increased hydrate dispersion stability 34–37%.
- Corrosion inhibitors decreased peak emulsified water droplet diameter by 20%.

GRAPHICAL ABSTRACT
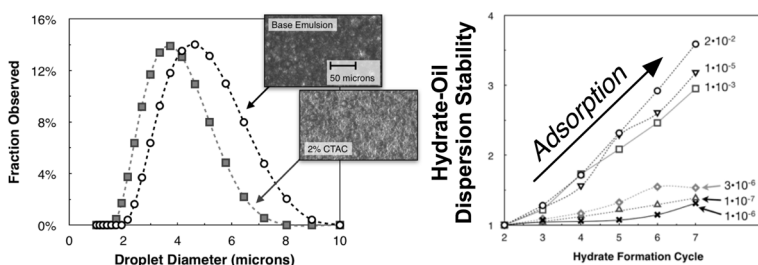
ABSTRACT

The stabilities of water–oil emulsions and hydrate–oil dispersions are critical parameters for assessing the risk of hydrate plug formation. These stabilities may be affected by the injection of chemicals designed for hydrate inhibition, but little is known about the impact of corrosion inhibitors on the formation of hydrate plugs; some corrosion inhibitors are chemically similar to hydrate anti-agglomerants, and are often used in similar concentrations. A new experimental method for studying dispersion stability is presented in which successive cycles of hydrate formation and dissociation from water–oil emulsions are measured with a differential scanning calorimeter over a broad range of inhibitor (surfactant) concentration. As the emulsion is taken through successive temperature cycles in which hydrate is formed and dissociated, the amount of heat exchanged with the environment per cycle decreases as the emulsion destabilizes and average water droplet size increases. A surfactant that stabilizes the emulsion results in a smaller decrease in the measured heat exchange per cycle, and the extent of this reduction can be used to quantify the surfactant's efficacy in stabilizing the emulsion. For a water–oil emulsion with no surfactant added, the cumulative heat flow decrease over seven serial hydrate dissociation trials was approximately 70%. The addition of either centrylpyridium chloride (CPC) or cetyltrimethylammonium chloride (CTAC) surfactants at or above 1×10^{-5} mass fraction in the oil phase eliminated this heat flow decrease, indicating the emulsion remained stable through all hydrate formation and dissociation cycles. For mass fractions of either chemical below 1×10^{-5} the heat flow decrease was the same as for the baseline experiment. We propose that this threshold corresponds to the concentration in oil required to enable sufficient adsorption of the corrosion inhibitor to the water–oil and hydrate–oil interfaces for it to act as an anti-agglomerant.

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1. Introduction

Gas hydrates are ice-like solids, where molecular cages of water surround light hydrocarbon components at high pressure and low

* Corresponding author. Tel.: +61 8 6488 3078; fax: +61 8 6488 1024.
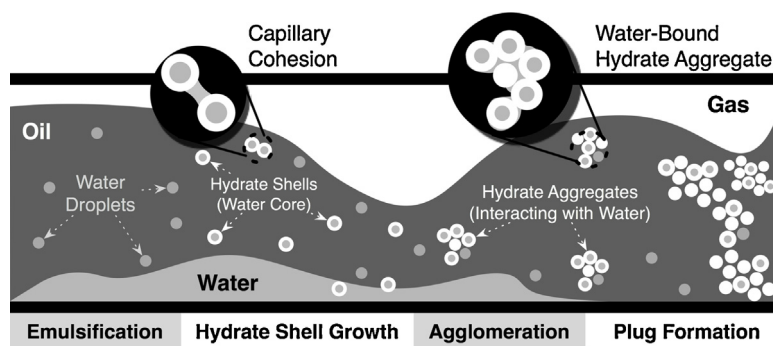*E-mail address:* zachary.aman@uwa.edu.au (Z.M. Aman).

Fig. 1. Conceptual picture of hydrate plug formation, adapted from Turner et al. [2].

temperature [1]. Hydrate formation represents a significant risk in deepwater oil production, where cooling process fluids may enter the hydrate equilibrium region. In cases of extended cooling, such as pipeline shut-in at high pressure, hydrate growth may result in rapid blockage formation on restart. Turner et al. [2], in collaboration with J. Abrahamason, introduced a four-step mechanism to describe hydrate plug formation in oil-dominant systems (Fig. 1): (i) water emulsification in a liquid hydrocarbon phase [3]; (ii) hydrate nucleation at the oil–water interface, which may be interpreted by molecular simulation studies [4]; (iii) capillary interaction between hydrate particles [5] and deposition of hydrate particles to the wall [6,7]; and (iv) jamming-type failure of large aggregates exposed to a decreasing flow annulus [8].

The risk of hydrate plug formation has traditionally been managed through the injection of thermodynamic hydrate inhibitors (THIs), such as alcohols (e.g., methanol) or glycols (e.g., monoethylene glycol) [9]. The volume of THI required scales directly with the amount of water produced and the operating pressure, and may limit the production viability of marginal assets. Creek et al. [10] estimated the cost of continuous methanol dosage at 30 USD per barrel of water produced. These costs have motivated two alternative hydrate management strategies collectively known as low-dosage hydrate inhibitors (LDHIs) [11]: (i) kinetic hydrate inhibitors; and (ii) hydrate anti-agglomerants (AAs). Both LDHI approaches allow hydrate to nucleate but introduce limitations that prevent small hydrate crystals from growing into plugging-type aggregates. Kinetic hydrate inhibitors are molecules or polymers with surfactant-type properties [12] that are believed to hydrogen bond to the growing hydrate crystal [13], decreasing the hydrate growth rate [14,15] for a limited range of subcooling below the hydrate equilibrium temperature [11].

As the appearance of a free water phase may result in water-coated hydrate particles with large aggregation forces, the use of physical or chemical modifications to produce a fine water–oil emulsion may decrease the overall risk of hydrate plug formation [5]. As aggregating hydrate particles exclude volume (i.e., have a fractal dimension below three), a fine particle slurry results in an optimal relative viscosity [17]. Anti-agglomerants are surfactant-type chemicals intended to reduce the aggregation potential of hydrate particles, resulting in a fine hydrate slurry [16]. Typical AA chemistries are quaternary ammonium salts [18]: recent advances in the development of AAs have attempted to minimize undesirable secondary effects such as stabilizing the water-in-oil emulsion [19] and/or reducing the quality of water that must be discharged to the environment [20]. Typical AA dosage quantities are on the order of 1–3 wt% depending on the water cut and were reported by Gao to become more effective at high salinity conditions [21]. The effectiveness of AAs has been attributed to the decrease they cause in the water–oil interfacial tension [22], which weakens the capillary bridge forces [23] that bind hydrate particles into aggregates [24]. Without the ability to aggregate, the effect of hydrate particles on slurry viscosity (and pressure drop associated with its flow) is minimized [17,25].

Lo et al. [26,27] suggested that ionic-type AA surfactants may also adsorb to the hydrate–oil interface, and inferred a transition from monolayer to bilayer adsorption at high surfactant concentrations. Aman et al. [28] observed a similar adsorption-type behavior for nonionic surfactant at the hydrate–oil interface, and used a Gibbs adsorption isotherm to estimate the packing density of adsorbed surfactant at the hydrate–oil interface from the dependence of the hydrate–oil interfacial tension on surfactant concentration in the oil [29]. The ionic surfactant basis for many AAs, which enables their strong adsorption to hydrate–oil interfaces [26], can make them also suitable for corrosion inhibition. Experimental studies by Alapati et al. [30] demonstrated the successful application of AAs to reduce the corrosion rate of carbon steel exposed to high-salinity brine.

The prospective use of established corrosion inhibitors (CIs) to minimize hydrate agglomeration is an outstanding question that forms the motivation for this investigation. Existing experimental methods to identify surfactant adsorption at hydrate–fluid interfaces are time-intensive and operate at atmospheric pressure. The novel calorimetric technique described here may allow experimentalists to assess surfactant adsorption at hydrate–oil interfaces at high pressure. For example, combining calorimetric results with high-pressure water–oil interfacial tension measurements as a function of surfactant concentration provides information on surfactant hydro- vs. hydrate-philicity. This study further probes whether simple corrosion inhibition chemistries may be used for basic anti-agglomerant properties in gas hydrate systems.

2. Materials and methods

Water-in-oil emulsions were prepared using 30 vol% deionized water added dropwise to a sterile schott bottle containing a crude oil and then homogenized at 20,000 RPM for 5 min; this process is similar to that prescribed by Sjöblom et al. [31] to generate crude oil emulsions with repeatable behavior. Each emulsion was allowed to 'ripen' for 24 h prior to measurement but was not used after 48 h of creation. The crude oil used in this study formed a stable water-in-oil emulsion for up to 70 vol% water and approximately 14 days as identified from macrophase separation in bottle stability tests [31]. At 20 °C, the dead crude oil's specific gravity was 0.85 and its viscosity was 4.7 cP at 3000 s^{-1} (measured with a ThermoScientific Haake VT550 rheometer).

2.1. Differential scanning calorimetry

The cyclic stability of water–oil emulsions and hydrate–oil dispersions was measured using a multi-cell differential scanning