

Can Micelles Be Used to Expedite and Enhance Laboratory Qualification Testing?

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ABSTRACT

The formation of corrosion inhibitor micelles in produced water can be used as an indicator of optimal dosage in a system. Prior to field use, tests are conducted in the laboratory on the relevant corrosion inhibitor, ideally in the presence of field hydrocarbon and other production chemicals. This ensures that the chemical and system are suitable and gives confidence that micelles will be detected, if present. During this pre-deployment testing, a corrosion inhibitor concentration series is created to determine the critical micelle concentration (CMC), i.e. the concentration at which micelles form for a given system. Other information is also provided, such as partitioning and potential influence of production chemicals on micelle formation.

Lab qualification testing of corrosion inhibitors require significant time, instrumentation, and skilled staff. Work has been conducted to determine if micelles can provide a higher throughput for compatibility testing so that more chemicals can be tested in the same timeframe, for the same cost; initial results are shown. The relationship between CMC and the field dose ultimately chosen is also considered. The usefulness of this approach, as a complementary qualification tool to those already used, is discussed in the context of being one that enables higher throughput testing and allows more chemicals to be screened for a more comprehensive and quicker process.

Key words: micelle, corrosion inhibitor, laboratory qualification, CMC, compatibility, partitioning

INTRODUCTION

The prevention of internal corrosion remains a significant challenge during the production of oil and gas. The use of film forming corrosion inhibitors is an important and cost-effective means of protecting assets from corrosion. These chemicals operate by forming a protective layer between the corrosive species present in the produced fluids and the pipe surface¹.

Prior to the use of film forming corrosion inhibitors in the field, the chemical must first undergo qualification testing in the laboratory. These chemical tests will inform the operator on the chemical performance, characteristics, and interactions with other production chemicals. Carrying out many of these tests can take a significant amount of time². For example, a simple linear polarization resistance (LPR) test to determine corrosion inhibitor performance can run for up to 16 hours. If the dose rate is unknown, then many of these tests may be carried out to narrow down to the required concentration.

Completing chemical qualification tests is essential and should not be avoided. Incomplete or unsuitable testing can lead to unforeseen issues when the chemical is used in a field environment. This leads to the question: if chemical qualification testing can't be avoided, can the process be streamlined?

This paper explores whether the properties of the surfactant components of film forming corrosion inhibitors can be exploited to streamline chemical qualification. Surfactants have the ability to form nanoscale aggregates, known as micelles, if certain criteria are met. Most importantly, the surfactant must be present in high enough quantities to form micelles; the point at which there is enough present is termed the critical micelle concentration (CMC)³. The CMC has been shown to signpost the point at which film forming corrosion inhibitors have reached an optimal concentration, indeed there is a published link between the CMC and optimal field dose^{4,5}.

The paper seeks to establish whether the presence of micelles can be used to streamline and improve current chemical qualification testing. The benefits of using surfactant micelles to inform on optimal field dose, chemical partitioning, field behavior, and compatibility with other chemicals will be discussed. Each of the experiments detailed below contains a discrete package of work, conducted to ascertain the behavior of the corrosion inhibitor under specific conditions. The corrosion inhibitors used were experiment-specific and generally contained amines (e.g. imidazolines and quaternary amines) amongst their active ingredients.

The micelle detection method described in the paper involves the addition of a proprietary reagent to the sample, followed by interrogation of the fluids by an optical detection technology⁶. The described micelle method is traditionally field-based⁷, meaning the same method can be used in the field as was used in the laboratory. This is advantageous, as comparable results can be generated and then fed back into additional laboratory experiments as required. This also offers a valuable insight into the transfer of laboratory testing to real-world field scenarios, providing results that can be used to inform future work.

EXPERIMENTAL PROCEDURE

Critical Micelle Concentration Determination

A critical micelle concentration (CMC) test was conducted by preparing a concentration series for a corrosion inhibitor, CI-1 (amine derivative as active ingredient), in a synthetic field brine (ca 137 g/L total dissolved solids). The samples were prepared at concentrations of 0-80 ppm in 10 ppm increments. The prepared solutions were shaken vigorously after chemical addition, before being allowed to settle for ca 1-2 hours. The samples were mixed with a proprietary marker and then analysed using an optical analyser. Data algorithms were applied to the raw data to determine the concentration at which micelles formed.

Corrosion Inhibitor Partitioning

A chemical partitioning test was conducted by preparing concentration series for the corrosion inhibitors, CI-2 (imidazoline and quaternary amines as active ingredients) and CI-3 (imidazoline and quaternary amines as active ingredients), in 100% model brine and in a 9:1 (v/v) mix of model brine and model oil. The model brine was NaCl (1 M) and the model oil was petroleum ether b.p. 180-280°C. The samples were prepared at concentrations of 0-100 ppm in 20 ppm increments (based on total fluid volume). The prepared solutions were shaken vigorously after chemical addition, before being allowed to settle for ca 1-2 hours. An aliquot of the aqueous phase was removed from each of the samples, mixed with a proprietary marker and then analysed using an optical analyser. Data algorithms were applied to the raw data to determine the concentration at which micelles formed, for all samples sets. By comparing the CMC between the samples without and with oil, the preference for aqueous or organic partitioning was established.

Field Simulation

A simulation was conducted in the laboratory to establish the behavior of a chemical under field-like conditions. A synthetic field brine was prepared and used as the aqueous phase. The organic phases used were either a model oil (petroleum ether b.p. 180-280°C) or a sample of untreated field hydrocarbon. Samples of field corrosion inhibitor, CI-4 (amine derivative and quaternary amine as active ingredients), were prepared from 0-100 ppm in 20 ppm increments (based on total fluid volume) in either 3:2 (v/v) solutions of synthetic brine and model oil or 3:2 (v/v) synthetic brine and field oil. The range of each sample set was extended with a 250 ppm sample during the experiment. All samples were shaken vigorously after chemical addition, and then heated for ca 1-2 hours at field temperature (80°C). The samples were allowed to cool slightly before the aqueous phases were drawn off into clean vessels. The samples were allowed to fully cool at this point to ambient room temperature (ca 1 hour). The cooled aqueous phases were mixed with a proprietary marker and then analysed using an optical analyser. Data algorithms were applied to the raw data to determine the concentration at which micelles formed, for both sample sets. Selected samples were also analysed for amine residuals using a commercially available test kit.

Corrosion Inhibitor Interaction with Other Production Chemicals

A kettle test using linear polarization resistance (LPR) was conducted using a corrosion inhibitor, CI-5 (imidazoline as active ingredient), at 25, 50 and 100 ppm. Three separate cells were used, one for each chemical concentration. The conditions were 50°C, with a 2 hour pre-corrosion and an X65 carbon steel (UNS K03014) coupon. The gas was CO₂ and the brine NaCl (1 M). The corrosion rate was measured over 15 hours. The preceding test was repeated with the addition of 25 ppm scale inhibitor (SI) to the LPR cells. Micelle measurements were taken from the subsamples of fluid taken from the cells, during and after the test. The subsamples were mixed a proprietary marker and then analysed using an optical analyser. Data algorithms were applied to the raw data to determine the concentration at which micelles formed, for both chemical and conditions.

RESULTS

Critical Micelle Concentration Determination

The CMC of a corrosion inhibitor can be used to determine the optimal dose for additional laboratory tests, e.g. LPR measurements. By measuring the CMC in advance, the range of concentrations to be tested can be reduced, saving time and improving efficiency.