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Formulation of Corrosion Inhibitors Using Design of Experiment (DOE) Methods and Discovering Highly Performing Inhibitors by High Throughput Experimentation (HTE) Methods Using Critical Micelle Concentration

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ABSTRACT

Critical micelle concentration (CMC) is a known indicator for surfactants such as corrosion inhibitors ability to partition from two phase systems such as oil and water. Most corrosion inhibitors are surface active and at critical micelle concentration, the chemical is partitioned to water, physisorb on metallic surfaces and form a physical barrier between steel and water. This protective barrier thus prevents corrosion from taking place on the metal surface. When the applied chemical concentration is equal or higher than the CMC, the chemical is available in aqueous phase, thus preventing corrosion. Therefore, it was suggested that CMC can be used as an indicator of optimal chemical dose for corrosion control¹. The lower the CMC of a corrosion inhibitor product, the better is this chemical for corrosion control as the availability of the chemical in the aqueous phase increase and therefore, can achieve corrosion control with less amount of chemical. In this work, this physical property (CMC) was used as an indicator to differentiate corrosion inhibitor performance.

The corrosion inhibitor formulations were built out by using combinatorial chemical methods and the arrays of chemical formulations were screened by utilizing high throughput robotics²⁻⁴,

using CMC as the selection guide. To validate the concept, several known corrosion inhibitor formulas were selected to optimize their efficacy. Each formula contained several active ingredients and a solvent package. These raw materials were blended in random but in a control, manner using combinatorial methodologies. Instead of rapidly blending a large number of formulations using robotics, the design of control (DOE) methods were utilized to constrain the number of blends.

Once the formulations were generated by DOE method, using Design Expert software that can effectively explore a desired space. The development of an equally robust prescreening analysis was also developed. This was done by using the measurements of CMC with a high-throughput screening methodology. After formulation of a vast array of formulation by using Design Expert software, the products were screened for by CMC using automated surface tension workstation. Several formulations with lower CMC than the reference products were selected.

The selected corrosion inhibitor formulations were identified and blended in larger scales. The efficacy of these products was tested by classical laboratory testing methods such as rotating cylinder electrode (RCE) and rotating cage autoclave (RCA) to determine their performance as anti-corrosion agents. These tests were performed against the original reference corrosion inhibitor.

The testing indicated that several corrosion inhibitor formulations outperform the original blend thus validating the proof of concept.

Keyword: High Throughput Screening, Design of Experiment (DOE), Combinatorial Chemistry, CMC, RCE, RCA

INTRODUCTION

Combinatorial chemistry, in which vast arrays of chemicals are generated randomly and screened them for a property of interest to optimize the property, has been around more than fifty years¹⁻². This methodology is used in pharmaceutical industry and especially in new drug discovery rather successfully. In new materials discovery, a vast number of new chemicals were synthesized using rapid synthesize and quickly screen them for qualitative trends for the desired property. From selected property, one might select the optimum property in the desired space. It is the combination of large and rapid chemical synthesis and high throughput screening with large scale data analysis methods constitute the backbone of combinatorial chemistry.

It is beginning to realize that the vast majority of variant development and high-throughput screening of thousands of compounds along with a vast amount of data handling is difficult. Recursive deconvolution strategies employed in identification of the most effective variants, may not produce a successful outcome. Therefore, it is thought that developing thousands of variants randomly may not be a suitable solution. This can be avoided by logically reducing the number of variants in front. Instead of rapidly blending a large number of formulations using robotics, the design of control (DoE) methods using Design Expert software can be utilized to constrain the number of chemical blends. Design of experiments (DoE) is the application of geometric principles to statistical sampling to obtain desired results such as minimizing the

number of experiments necessary to obtain the answer to a problem or minimizing the variance of estimated coefficients obtained through regression. Thus, DoE experiments can reduce thousands of possible variants to more manageable and more meaningful less than 50 variants. In this work, we used software program called Design of Experiment to manage the combinations of formulations.

In the oil and gas industry, there is an increasing focus on prevention corrosion of metal goods downhole as well as flowlines. There are several ways to prevent internal corrosion and one of the most widespread methods is to introduce corrosion inhibitors to a corrosive environment. A corrosion inhibitor is defined as a chemical substance that, when add in small quantities to an environment, effectively checks, decreases, or prevents the reaction of metal with the environment. There are several approaches to prevent internal pipeline corrosion including; changing the material in the system, changing the environment or introducing a barrier between the materials and the environment such as a coating or a corrosion film. One or more of the above conditions can be combined in developing good corrosion inhibitors. The class of corrosion inhibitors known as the Film Forming Corrosion Inhibitors prevent corrosion by forming a thin film on the material surface, which acts as a barrier for corrosive species such as acidic water when coming into contact with the metal surface. Thus, preventing or reducing corrosion in oil and gas carrying pipelines.

It is not easy to develop cost-effective and high performing corrosion inhibitors. It is well known that environmental components such as carbon dioxide, hydrogen sulfide, oxygen and dissolved salts affect corrosion attack. Bacteria, solids, flow regime, temperature, pressure, oil-water ratio, organic acids, elemental sulfur, polysulfides, pH and material type also can be a factor in corrosion control. Another important factor that is becoming exceeding important is the toxicity of the chemicals. This is especially true for offshore and deepwater chemical applications, where the eco-toxicity of the chemicals is important as the produced water with the chemicals is discharged to sea Inhibitors for sub-zero environments, extremely high temperatures and pressures, extremely sour conditions with elemental sulfur and green chemistry are desired as the chemical currently available are expensive or not effective or both. Developing new chemistries and formulating them for these difficult environments are challenging. Automated these processes using combinatorial chemistry and high throughput screening is a good, fast and effective solution for these difficult and time-consuming problems⁵.

In this work, critical micelle concentration (CMC) is used as the screening tool for high throughput screening. Corrosion inhibitors are surfactants and therefore, operate at the interface such as oil and water. Increasing inhibitor concentration can increase the inhibitor concentration at the interface thus reducing surface tension. At CMC, the interface is saturated, and any added inhibitor would move to bulk water phase where hydrocarbon part of the molecule gets aggregated to minimize energy. In this cluster, the relative water-insoluble hydrocarbon part of the molecule is aggregated while the more water-soluble part of the molecule orient towards the bulk water. The middle of the cluster is lipophilic and outer layer is hydrophilic. This minimizes the unfavorable energy repulsions. In hydrocarbon phase, the orientation is reversed, and hydrophilic section of the molecule is aggregated in the middle of the three-dimensional structure. The maximum efficiency of inhibitors is reported to be near their CMC. It is assumed that below CMC, there are inhibitor molecules adsorbed on the metal surface. However, when the micelles form above CMC, excess inhibitor results in the formation

of micelles which does not significantly alter corrosion rate. Therefore, CMC is understood to be an important parameter in determining the effectiveness of corrosion inhibitors.

The CMC can be measured using the interfacial tension method. This is a straightforward method and CMC is determined by increasing inhibitor concentration and measuring interfacial tension. At CMC, the interfacial tension becomes constant with increasing dose rate. In this work decreasing CMC of a product is assumed to be associated with decreasing corrosion rate.

EXPERIMENTAL PROCEDURE

High Throughput Approach

A phosphate ester-based corrosion inhibitor formulation (**Corrosion Inhibitor 12035**) was selected as the reference product for optimization. A large array of products was blended using an automated Swing Formulator followed by automated surface tension screening. Fourteen experimental blends were selected from high throughput screening that has lower CMC than the reference chemical. These chemicals were tested by classical lab methods such as rotating cylinder electrode (RCE) and by rotating cage autoclave (RCA) test methods.

RCE Test

The RCE experiments (Figure 1) were conducted in glass reaction kettles. These kettles contained 760 mL of 3.0 % NaCl solution (brine) and 40 mL of synthetic oil. This combination of brine and oil was continuously purged with the premixed gas and heated to 70°C. Flow meters were used to ensure the premixed gas flow rates were identical between reaction kettles. A magnetic stir bar and hot plate combination were used to agitate the solution and control the reaction temperature. When the RCE was inserted in the kettle, it went through the oil layer and into the brine. Then, a constant rotation rate of 3000 RPM was applied. After this, the RCE never contacted the oil again. The magnetic stirrer was stopped to allow the RCE to control the hydrodynamic of the brine. The rotation rate was kept constant during the experiment. This generated a wall shear stress of 10 Pa. The working electrode was made of carbon steel C1018 (UNS G10180) cylinder with a surface area of 3.16 cm². A Hastelloy C276 (UNS N1010276) electrode was used as a pseudo-reference. A titanium rod (UNS R50400) was used as the counter electrode. Linear Polarization Resistance (LPR) measurements were made with a potentiostat designed for corrosion measurements. The voltage perturbation was ± 5 mV over the open circuit potential. A constant **B** value of 26 mV/dec was arbitrarily selected. This is because these experiments were performed only to compare the different inhibitor's performance. A multiplexer was used to execute several experiments in series. The corrosion rate was measured for all the RCEs in the kettles. When the corrosion rates were similar for all RCEs (after 2 hours pre-corrosion time), a 5 ppm of each inhibitor was injected.



Figure 1. RCE test equipment

HPHT Performance Tests – Rotating Cage Autoclave

To ensure the products perform in a variety of flow conditions, both low and high shear conditions were emphasized to test the product performances in different flow regimes. The lower shear (up to 40 Pa) tests were performed using 1-liter RCAs. In RCA testing, three weight loss coupons fixed on the rotating cage were used in each autoclave. The coupon shafts rotated at 1,000 RPM, which corresponded to a 40 Pa shear stress. The autoclaves were run at 70°C and the partial pressures of gas matched to those experienced in the field. General corrosion rates were calculated by weight loss measurement. The autoclave setup is shown in Figure 2.

Test conditions have been summarized below.

Temperature	70°C (158°F)
Gas Composition	57psi CO ₂
Pressure	total = 57psi CO ₂ + H ₂ O vapor
Fluid Composition	3% NaCl Synthetic brine
Dose Rate	60 ppm based on total fluids
Stir Rate	1,000 RPMS
Test Duration	7 days