

**Corrosion Inhibitor Surfactant Optimization:
Part 1 – Inhibitor Efficiency**

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ABSTRACT

A homologous series of alkyldimethylbenzylammonium chlorides (BAC) was used as a model for a composite commercial corrosion inhibitor formulation. The homologous series consisted of three BACs with C₁₂, C₁₄ and C₁₆ tail lengths. A 10-point, three-component mixture design experimentation was performed to determine the composition for achieving the ‘optimal’ corrosion inhibitor performance. The CMC of each mixture combination (single, binary or ternary) was firstly evaluated using the lipophilic dye Nile Red. The corrosion inhibition performance of each mixture was subsequently determined at the respective CMC in a 1 wt.% NaCl solution under approximately 1 bar partial pressure of carbon dioxide (CO₂) at 30 °C. In order to calculate the corrosion inhibitor efficiency for each mixture of components, the corrosion rates before and after the injection of the corrosion inhibitor mixture were measured by linear polarization resistance (LPR). The measured CMC values and corrosion inhibitor efficiencies for each mixture were plotted on a ternary diagram and a cubic response curve fitted to each dataset. The ‘peak’ in the mixture CMC response curve and the peak in the corrosion inhibitor efficiency response curve were then compared, and an optimal composition was estimated from the mixture response analysis.

Key words: Surfactant, Critical Micelle Concentration, Inhibition, Optimization

INTRODUCTION

Background

Corrosion inhibitors provide a critical barrier to internal corrosion, presenting the most cost-effective form of mitigation and enabling operators to use carbon steel where it would otherwise be impractical. The correct selection and validation of inhibitors is essential to ensure successful field deployment, providing safe and reliable operation. However, the selection and optimization of a corrosion inhibitor for a particular field application is not trivial.

Many corrosion inhibitors are organic amphiphilic surfactants, featuring a hydrophilic head group and a hydrophobic hydrocarbon tail. In solution, the surfactant monomers exhibit adsorption to surfaces, with the hydrophobic tail of each monomer extending into the solution to provide a physical barrier between the substrate and the corrosive electrolyte.

As the concentration of surfactants within a solution increases, a greater number adsorb to the surface, reducing interfacial tension. Once a specific concentration of surfactants is reached, the monomers begin to aggregate. In an aqueous solution, these spheroidal shaped aggregations of monomers (or 'micelles') are structured such that the tails point toward the center of the micelle, and the head groups point outwards into the solution. The concentration at which micelles are first detected in the solution is termed the Critical Micelle Concentration (CMC).

The CMC is analogous to a solubility limit of the surfactant monomer concentration, as the micelles form a separate pseudo-phase. Below CMC, the surfactant concentration is equal to the monomer concentration in solutions, and all surfactants exist in their monomeric form. Above CMC, a portion of the total surfactant concentration consists of micelles, with the remainder existing as monomers. Any further addition of surfactant to the solution results in the increase in micelles, whilst the monomer concentration remains fixed. It is believed that monomers adsorption to the surface is largely responsible for the provision of a physical barrier. It has therefore been suggested that the CMC provides an indication as to a transition in performance vs surfactant total concentration¹. Figure 1, adapted from Wang and Free provides an illustration of this relationship.¹

Recently, Moradighadi and co-workers have investigated the relationship between CMC and corrosion rate.² In their study, the corrosion rate was measured with increasing concentration of surfactant until a minimum corrosion rate/maximum efficiency was reached. This concentration was termed the Metal Surface Saturation Concentration (MSSC). It was suggested that the maximum inhibitor performance would occur when the metal surface was fully saturated with inhibitor, and a further increase in coverage or reduction in corrosion rate was not attainable. In this work, the authors typically found that the MSSC was below the CMC, and as a result claim that the CMC is not an indicator of corrosion performance. However, a measured CMC is still an effective starting point as a means of understanding near-maximum inhibitor performance for a particular system, especially with MSSC standing below CMC.

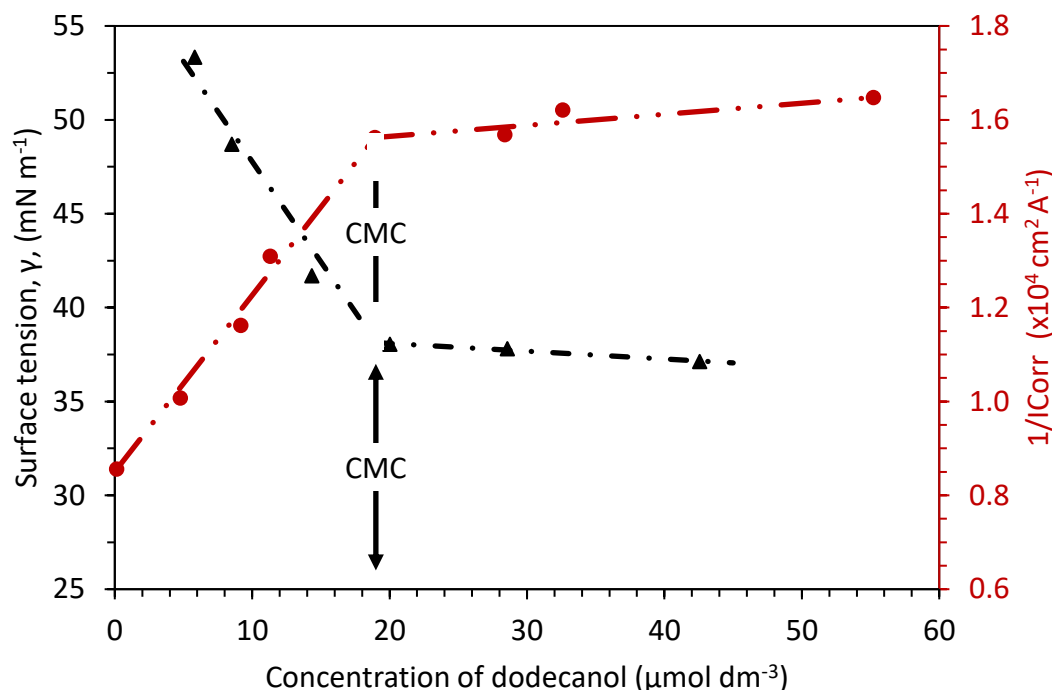


Figure 1: Correlation between CMC and corrosion inhibitor performance, redrawn from Wang and Free 2004.¹

In this study, the correlation between CMC and corrosion rate was assumed to hold and utilized as a methodology to assess the corrosion inhibition performance of a mixture experiment. The performance a mixed surfactant system was examined in relation to the system CMC and corrosion inhibition efficiency. The CMC of each of the components was measured using the lipophilic dye Nile Red.⁴ The values of CMC were used as the basis for a 10-point three-component mixture experiment to determine the composition for ‘optimal’ corrosion inhibitor performance. The three component 10-point design was a simplex-centroid design augmented with three interior points to determine the relative concentrations used in the mixture experiment.

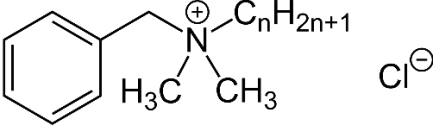
This paper describes a “traditional” approach to corrosion inhibitor composition optimization through the use of CMC and corrosion inhibitor efficiency measurements with the companion paper describing a adsorption kinetic approach.³ Part I of this paper reviews the CMC values of the various mixtures, modelling the data using a ternary mixture model fit to the experimental data points. The ternary fit can be used as a means of predicting the CMC of any mixture. This is then compared with the predicted CMC of the ideal mixture theory where no net interaction between the individual components is assumed. In addition, the corrosion inhibitor performance is reviewed based on the analyzed mixtures, and used as a means of extracting the estimated “optimal” inhibitor composition and performance.

EXPERIMENTAL PROCEDURE

Homologous Series

Three BAC molecules/components were used in this study, with C₁₂, C₁₄ and C₁₆ tail lengths. The general chemical structure of the three BACs are shown in Table 1. All surfactants were analytical grade and sourced from Sigma-Aldrich^{®,*}, with no further purification conducted.

Table 1: Homologous Series Description

Acronym	Full Name	n	Structure
C ₁₂	Benzyltrimethyl-dodecylammonium chloride	12	
C ₁₄	Benzyltrimethyl-tetradecylammonium chloride	14	
C ₁₆	Benzyltrimethyl-hexadecylammonium chloride	16	

Surfactant CMC Characterization and Mixtures

Surfactants in most industrial applications are mixtures with molecules of various tail lengths present, as opposed to a pure-single component. In theory, for the ideal case the CMC is determined by the CMCs of the single components present, and the mole fractions of each component in the mixture. For an ideal mixture, with no net interaction between different components, the CMC of a ternary mixture can be estimated from the CMC of the pure components using,⁵

$$\frac{1}{CMC_{Mix}} = \frac{x_1}{CMC_1} + \frac{x_2}{CMC_2} + \frac{x_3}{CMC_3} + \dots \quad [1]$$

Where, x_i is the mole fraction of component i and CMC_i is the CMC of component i .

CMC Experimental design and solution preparation

The CMCs of each component inhibitor and seven multi-component mixtures of the inhibitors were measured following a ternary mixture experiment design from Snee.⁶ The CMC was measured using a spectrophotometric method involving the lipophilic dye Nile Red; this method was selected as the dye probes the micelles directly rather than relying on surface tension as a proxy for micelle detection.⁴ Table 2 shows the mole fractions of each component for the 10 chosen experiments. Runs 1 - 3 are the pure components, and runs 4 - 10 are multi-component mixtures, with runs 4 - 6 being binary mixtures and runs 7 - 10 being ternary mixtures.

* Trade Name

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Table 2: Ten run design of mixtures, adapted from Snee.⁶

Mixture Number	Mole Fractions		
	C ₁₂	C ₁₄	C ₁₆
1	1	0	0
2	0	1	0
3	0	0	1
4	½	½	0
5	½	0	½
6	0	½	½
7	⅓	⅓	⅓
8	⅔	⅙	⅙
9	⅙	⅔	⅙
10	⅙	⅙	⅔

The test solution was prepared from a concentrated inhibitor stock solution with typically ten times greater concentration than the highest sample concentration evaluated in each mixture experiment. Given the reversible nature of micelle formation, this is a valid approach, providing that the various test solutions formulated at lower concentrations were afforded enough time to re-equilibrate.

To achieve the desired concentration, each sample was prepared by weighing out a minimum required mass of inhibitor in a 250 mL beaker, dissolving in the appropriate volume of 1 wt.% NaCl brine solution at pH 4 (set using 1M hydrochloric acid). The inhibitor was dissolved in the solution at 30°C using a magnetic stirrer to ensure full dissolution.

In order to prepare the multi-component inhibitor mixtures, the mole fractions of each inhibitor were converted into mass fractions using Equation [2],

$$Frac_{mass,i} = \frac{Frac_{molar,i} M_i}{\sum_{i=1}^{i=3} Frac_i M_i} \quad [2]$$

where $Frac_{mass,i}$ is the mass fraction of component i in a mixture, $Frac_{molar,i}$ is the mole fraction of component i in a mixture and M_i is the molar mass of component i . A minimum required mass of one inhibitor was weighed out and the appropriate masses of the other components were then carefully weighed out to achieve the desired mixture mass fractions, prior to dissolution in brine.

The concentrated stock solution was then combined with a 30°C, 1 wt.% NaCl solution at pH 4 in different ratios and mixed thoroughly for ≈ 15 minutes to achieve ~ 14 -20 samples with concentrations spanning two to three orders of magnitude. A 7 mL sample was taken from each of the brine solutions and placed into a sealed vial. A sample with no surfactant present was

also collected in order to initially 'zero' the spectrophotometer during measurements. All sealed vials were then stored in a water bath at 30°C for ≈ 1 h. This temperature was used to replicate the conditions used in the corrosion rate experiments carried out in a complementary study.

Nile Red addition and incubation

Nile Red dye was used to identify the absence or presence of micelles in each collected sample. Nile Red powder was dissolved in isopropanol to produce a 1000 μM concentration dye. 70 μL of dye was pipetted into each 7 mL vial (with the exception of the 'zero' sample). After addition of the dye, each vial was then shaken vigorously for >1 minutes and placed back in the water bath. After Nile Red had been added to the final sample, the vials were left to incubate in the water bath for 30 minutes before beginning measurements in the spectrophotometer. One minute was left between Nile Red addition into each sample to account for the time between spectrophotometer readings, to ensure consistent incubation times for every sample.

Spectrophotometer readings

A DR3900[†] Laboratory Spectrophotometer was used to determine the absorbance spectra for each of the ten mixtures outlined in Table 2 across the various concentrations tested. After 30 minutes incubation, the spectrophotometer readings began with the zero sample (containing no inhibitor) to calibrate/zero the spectrophotometer. The readings for all the inhibitor samples were then carried out in order of increasing concentration. Samples were poured into a cuvette and placed in the spectrophotometer which measured the absorbance of each sample across the visible light spectrum from 350-800 nm wavelength. A higher concentration of micelles in a sample would result in a greater aggregation of Nile Red. This effectively produces a greater intensity of solution colour that would absorb more light and result in a higher peak absorbance measurement. Peak absorbance was typically observed between 560-590 nm wavelengths.

Data Analysis / CMC Determination

The absorbance spectra for each sample was transferred from the spectrophotometer to a PC. Figure 2 shows a typical "waterfall" plot of an example of a set of spectra collected for Mixture 3 (BAC-C₁₆ alone).

[†] Trade Name

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