

Correlation Between Concentration of Maximum Adsorption on Platinum and CO₂ Corrosion Inhibition Efficiency of Nitrogen Heterocyclic Aromatic Compound

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ABSTRACT

Rotating cylinder electrode (RCE) methodology with electrochemical impedance spectroscopy (EIS) measurement was applied to study the inhibition behavior of pyridine, quinoline and acridine on CO₂ corrosion of X65 carbon steel. The inhibition performance of nitrogen heterocyclic aromatic compounds was evaluated as a function of the number of rings (single/double/triple), salinity (0.1%, 1%, 10% wt. NaCl), pH (4, 5, 6) and temperature (30°C, 50°C, 70°C). The chemical dosages were based on a series of proportional Concentrations of Maximum adsorption (CMA) values determined from a parallel study on Pt electrode, using a variety of other methodologies.

The results showed that acridine exhibits high inhibition efficiency while pyridine and quinoline exhibit no inhibition at studied conditions. The concentration for maximum inhibition efficiency (CME) and Langmuir adsorption constants (K_{ads}) were obtained for acridine and compared with their corresponding CMA values, as a function of pH, temperature and salinity.

Key words: RCE, inhibition, CO₂ corrosion, pyridine, quinoline, acridine, concentration for maximum adsorption, CMA

INTRODUCTION

Most of the CO₂ corrosion inhibition work that has been published has been based on constituents commonly used in oil and gas corrosion inhibitor formulations that behave as surfactants (short for surface-active agents). In surfactant inhibitors, like Quaternary Amines and Imidazolines, the amphiphilic nature of their molecular structure comprising hydrophobic groups (tails) and hydrophilic groups (heads) is responsible for adsorption at interfaces and micellization in bulk aqueous phases. For these compounds, correlations have been found between concentration for maximum inhibition efficiency (CME) and critical micelle concentration (CMC)^{1,2} and, more recently, concentration of maximum adsorption on platinum (CMA).^{3,4}

(1) Working at BP America when the work was conducted

A second type of molecule (e.g., Nitrogen Heterocyclic Aromatic Compounds) are also used as a constituent of inhibitor formulations. These compounds are not amphiphilic in nature and, therefore, cannot be characterized based on CMC. The mechanism for adsorption of these compounds and their corrosion inhibition of metals has been linked to the nitrogen heteroatom present or to the π electrons of the heterocycle ring. It leads to an adsorptive bond through a Lewis acid-base type interaction wherein the inhibitor acts as electron donor and the metal as the electron acceptor.

Molecules having a pyridine ring have been used as components of commercial inhibitors and are known themselves to be inhibitors.^{5,6} Pyridine, quinoline, and acridine have been reported to be corrosion inhibitors of Fe and steel in 5% HCl solutions at 25°C.⁷ In that study, the degree of inhibition was found to increase with the number of rings (i.e., acridine was the most potent inhibitor) and the authors suggested that the initial adsorption of inhibitor was a cooperative chemisorption process involving chloride. Other studies indicated quinoline to be an inhibitor, although various quinoline derivatives had better performance.^{8,9}

The mechanism for adsorption of these compounds and their corrosion inhibition of metals has been linked to the nitrogen heteroatom present in the molecule which is an electron-active center due to its lone-pair electrons. It leads to an adsorptive bond through a Lewis acid-base type interaction wherein the inhibitor acts as electron donor and the metal as the electron acceptor.^{10,11} Polarizability and electron density at this site affect the adsorption bond strength. In some studies, the corrosion inhibition mechanism has been attributed to protonation of the heterocycle ring and resulting transformation into intermediate species.¹²

Another research indicated that n-alkyl substituted derivatives of heterocyclic compounds behaved as good HCl corrosion inhibitors and that the inhibition efficiency increased with the length of the hydrocarbon chain of the n-derivatives and the number of aromatic systems. Improvement in inhibition efficiency was believed to result from inductive effects that enhance the electron density at the N-heteroatom and increase its interaction with the steel surface, as well as blocking effects from the non-polar, saturated alkyl chain.

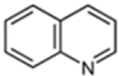
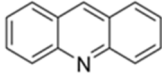
Pyridine, quinoline, and acridine were evaluated in a previous work and confirmed (by fluorescence and surface tension) not to exhibit micellization but adsorb on platinum, allowing the determination of CMA values as function of pH values, temperature and salinity.¹³

This paper shows the effectiveness of a homologous series of nitrogen heterocyclic aromatic compounds in mitigating CO₂ corrosion and discusses how the methodology developed to characterize inhibitors based on their CMA values is applicable to non-surfactant corrosion inhibitors.

EXPERIMENTAL PROCEDURE

The molecular structures of the three compounds evaluated in this work are shown in Table 1.

Table 1
Molecular Structure of Inhibitors Evaluated

Pyridine	
Quinoline	
Acridine	

The inhibitors were evaluated at up to three salinities (0.1%, 1% and 10% wt. NaCl), three temperatures (30 °C, 50 °C and 70 °C) and three pH values (4, 5 and 6). This work was part of a wider research program that included other model compounds, including quaternary amines and imidazolines. Table 2 summarizes the tests conducted and CMA values that were used as a reference for calculating the concentrations of inhibitor injections in this work. The intent was to examine a range of concentrations above and below the CMA, hence the range of concentrations tested were multiples of the CMA values in Table 2 and were at 0.1X, 0.3X, 0.5X, 1X, 3X, 5X and 10X CMC values. Duplicates were conducted at two of the CMA multiples to evaluate repeatability, which was found to be less than 10% from the average.

The initial CMA values were estimated based on a parallel study¹³, shown in Table 2 within parentheses. Some tests were conducted using CMA values higher than measured on platinum, to evaluate the effect of even higher concentrations.

The experimental method is the same as previous studies conducted on quaternary amines and imidazolines, and reproduced below.^{3,4}

Electrochemical Impedance Spectroscopy (EIS) testing was performed using a three-electrode configuration in a glass cell, which consisted of a rotating cylinder as working electrode (RCE), platinized niobium wire coil as counter electrode, and silver/silver chloride (saturated KCl) as reference electrode. The working electrode was made of API X65 carbon steel, with an outside diameter of 1.5 cm and exposure surface area of 3.0 cm². The electrode was freshly polished (600 grit silicon carbide paper), cleaned, dried and mounted on the RCE rotor on the day of the test. All the tests were conducted at 2000 RPM rotation rate, which correlated to a wall shear stress (WSS) of approximately 8 Pa.

Table 2
Evaluated Test Conditions and CMA values used as a center point for the range of concentrations studied (CMA measured on Platinum¹³ within parenthesis).

Nominal pH	Temperature						
	30°C	50°C			70°C		
	Salinity	Salinity			Salinity		
	1.00%	0.10%	1.00%	10.00%	0.10%	1.00%	10.00%
Pyridine - Used CMA Values, μM (Measured CMA on Pt) 1 μM = 0.079 ppm							
5	100 (8)						
Quinoline - Used CMA Values, μM (Measured CMA on Pt) 1 μM = 0.129 ppm							
4	128 & 1280 (128)					512 (512)	
5	256 (256)						
6	64 (64)						
Acridine - Used CMA Values, μM ((Measured CMA on Pt) 1 μM = 0.179 ppm							
4	20 (8)		20 (1)			20 (0.5)	
5	20 (4)	30 (1)	20 (4)	10 (1)	30 (1)	2 & 20 (1)	10 (1)
6	5 (1-2)		20 (4)			20 (0.5)	

The overall test set up was configured to perform two tests in parallel in separate glass cells, using a Gamry Reference 600[†] potentiostat via an ECM8^{Error! Bookmark not defined.} electrochemical multiplexer for EIS measurements. The test cells were contained in a customized, acrylic enclosure which was purged with ultra-high purity N₂ throughout the test. The acrylic box and N₂-purging were used to minimize the ambient O₂ levels around the RCE setup, and thereby minimize oxygen intrusion into the test cells. It has been found that this type of enclosure is critical to assure low dissolved oxygen concentration in RCE tests.

The test solution was prepared by dissolving reagent grade NaCl in deionized water. Tests were conducted at three nominal pH levels: 4, 5 and 6. The nominal pH 4 was the natural pH of the CO₂ saturated solution without bicarbonates. Sodium bicarbonate was added to the NaCl solutions for the purpose of pH adjustment to pH 5 and 6 and introduce some buffering. The amount of sodium bicarbonate required for pH adjustment at the test temperature was determined using a thermodynamic model⁽²⁾. The solution was purged with research-grade CO₂ for at least 12 hours in a pre-conditioning vessel (PCV). Before the CO₂ was introduced into the PCV, it was passed through an oxygen scrubber. Before transferring the CO₂ saturated solution to the test cells, pH and dissolved oxygen concentration were measured. Dissolved oxygen was confirmed to below 10 ppb and pH within 0.1 units of the target pH. Prior to solution transfer, the assembled test cells with installed RCEs and the acrylic box were purged with ultra-high purity N₂. The purging gas in the test cells was changed to 100% CO₂ (research grade) after transferring 1 L pre-conditioned solution to each test cell. A condenser with circulating coolant was used to minimize water loss from the test cell. The temperature of the test solution in the test cell was maintained at the desired temperature (± 1 °C) by circulating hot water through the double walls of the test cells.

Open-circuit potential (OCP) and EIS measurements were performed every 15 minutes starting immediately after the solution transfer. After 90 minutes of this initial pre-corrosion stage (with 0 ppm inhibitor), four dosages of inhibitors were sequentially injected every 90 minutes. The inhibitor was prepared as a stock solution of an appropriate concentration so that between 0.1 and 1 mL of stock solution would be required for each injection phase. The inhibitor was injected directly into the test solution using a precision syringe and a long needle through a septum in the test cell. A pair of tests were performed at the same time to evaluate the same inhibitor at the same salinity and temperature conditions but with different inhibitor injection dosages. Inhibitor concentrations, hereafter mostly expressed as multiples of CMA (x CMA), were dosed as $\mu\text{L/L}$ (ppm). The injection schedule was designed to complete the evaluation of an inhibitor in an 8-hour work day, for up to seven concentrations ranging from 0.1 X CMC to 10X CMC, with the effect of each dosage being evaluated over a period of 90 minutes.

EIS measurements were performed on the RCE by applying a sinusoidal voltage of 10 mV (RMS) at OCP and varying frequency from 10,000 Hz down to 0.1 Hz. Polarization resistance (R_p), and solution resistance (R_s) were obtained from each EIS measurement by fitting the spectrum to an equivalent circuit. In many cases, a single time constant was observed, and data were fitted to a Randles' circuit as shown in Figure 1 (Model 1). In other cases, two-time constants were observed in the EIS data and fitted to an equivalent circuit with two constant phase elements (CPE), typically used for filmed surfaces (Figure 1, Model 2).

Corrosion rates (CR) were calculated from corrosion currents (I_{corr}) at open circuit potential (OCP). I_{corr} was determined from the R_p value according to equation (1) with a Stern-Geary constant $B = 0.027$ V, which has been found to suitable for carbon steel CO₂ corrosion.

$$I_{\text{corr}} = \frac{B}{R_p} \quad (1)$$

The determined corrosion rates at a series of inhibitor concentrations were used to calculate the inhibitor efficiency, assumed to be equivalent to the effective surface coverage according to Equation (2) below.

[†] Trade name.

⁽²⁾ Chemistry solutions and thermodynamic speciation software - OLI Analyzer Studio, OLI Systems, Inc.

This assumed that corrosion rate was inhibited due to the adsorption of the molecules of the inhibitor on the metal surface, as initially proposed by Hackerman et al.¹⁴

$$S = \left(1 - \frac{CR_i}{CR_o}\right) \times 100\% \quad (2)$$

Where,

S , surface coverage at a specified inhibitor concentration

CR_i , the steady-state inhibited corrosion rate at a specified concentration (at the end of 90-minutes testing period)

CR_o , the uninhibited corrosion rate at the end of 90-minute pre-corrosion stage. If CR_i was greater than CR_o , a negative surface coverage was reported.

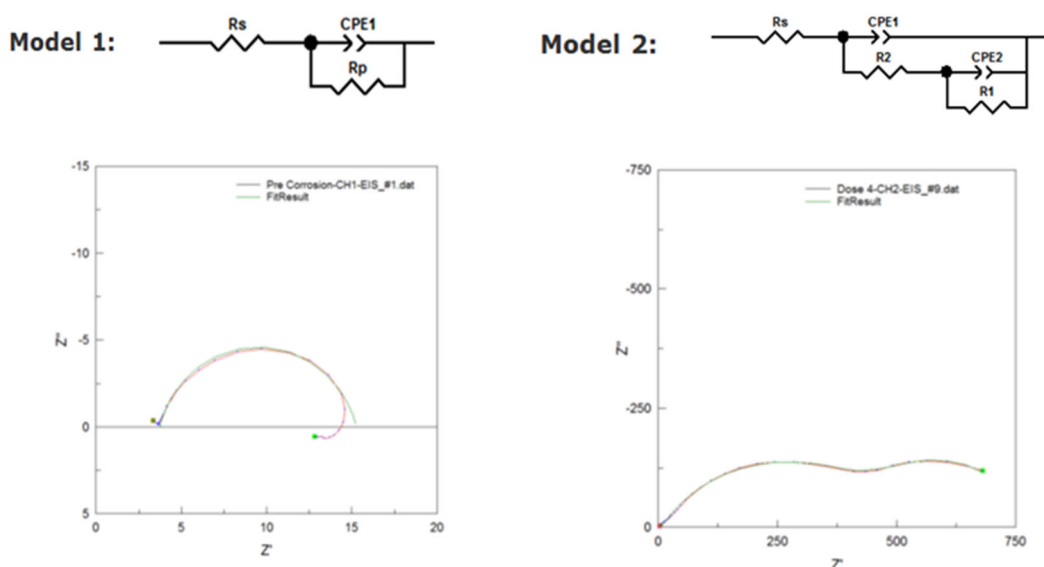


Figure 1: Example of the Nyquist plots of EIS with one time constant (left) and two-time constants (right). X65 steel in 1% NaCl at 70°C and pH ~4, with injections of acridine.

Several adsorption isotherms have been used to characterize inhibitor performance¹⁵. In the present work, the surface coverage data were fitted per the following Langmuir isotherm equation, which assumes there are no interactions between adsorbed molecules on the surface:

$$S = \frac{S_{max} \cdot K_{ads} \cdot [inh]}{1 + K_{ads} \cdot [inh]} \quad (3)$$

Where,

$[inh]$, inhibitor concentration, in units of multiplies of CMA, X CMA

S , effective surface coverage calculated from corrosion rate change caused by each inhibitor $[inh]$

S_{max} , the maximum surface coverage (fitting output)

K_{ads} , the adsorption constant (fitting output). The K_{ads} thus calculated had the units of CMA^{-1} . It was further converted to the units of μM^{-1} using the CMA value assumed for the test.

Since the adsorption isotherms were not produced from direct measurements of adsorption but derived from EIS data, the maximum inhibitor efficiency (equivalent to S_{max}) occurs at the inhibitor concentration at which all sites available for Langmuir adsorption are filled.