

On the Adsorption Properties of Non-Surfactant Corrosion Inhibitors: Pyridine, Quinoline and Acridine

Jose Vera
DNV GL (USA) Inc
Katy, TX, USA

William Durnie
BP Exploration Operating Company Ltd
Middlesex, UK

Ashwini Chandra, Kevin Ralston
DNV GL (USA) Inc.
Columbus, OH, USA

Richard Woollam⁽¹⁾
Richard C Woollam and Associates LLC
Katy, TX, USA

ABSTRACT

Most of the carbon dioxide (CO₂) corrosion inhibition work published has been based on constituents that behave as surfactants (e.g., quaternary amines and imidazolines). For these compounds, a relationship has been found between the concentration for maximum efficiency and the critical micelle concentration (CMC) and, more recently, with the concentration of maximum adsorption (CMA) on platinum.

This paper shows how the methodology developed to characterize inhibitors based on their CMA values is still applicable to non-surfactant corrosion inhibitors, which would not show a CMC.

The effects of parameters such as pH, salinity, temperature and number of rings in the molecules' molecular structure on the adsorption process of molecules having a pyridine ring (pyridine, quinoline, and acridine) were evaluated. Adsorption isotherms were determined under different solution conditions and were used to calculate thermodynamic constants – Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) change associated with this process. Additional studies were conducted to understand the effect of protonation on the adsorption properties of these molecules. The correlation between the CMA values obtained in this work and CO₂ corrosion inhibition will be presented in another paper.

Key words: Non-surfactant Corrosion Inhibitors, Concentration of Maximum Adsorption

INTRODUCTION

Corrosion inhibitors are widely used in the oil and gas industry to protect infrastructure from internal corrosion.¹ The most common types of corrosion inhibitors used in the oil and gas industry are primarily formulated based on organic molecules that have amphiphilic characteristics and are surfactants (short for surface-active agents).² These molecules are composed of at least two parts, including a highly polar or ionized functional group that is hydrophilic in nature (head group) and a hydrophobic (tail), which is usually a medium to long aliphatic chain.³

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

When surfactants are in solution, they decrease the energy of the system by segregating to surfaces such that the solubility of both hydrophobic and hydrophilic parts of their structure are satisfied. Above the Krafft temperature and certain surfactant concentration, the thermodynamically favorable configuration for the surfactant monomers is to form aggregates in solution that are termed “micelles”. In this case, the surfactant molecules orient themselves such that their hydrophobic tail is shielded from the aqueous medium. The formation of micelles can be used as an indication that other interfacial areas to which surfactants segregate towards are largely covered. This point is termed the “Critical Micelle Concentration” (CMC) and is the maximum concentration of inhibitor monomers (for a given set of environmental conditions) in which monomer is in equilibrium with the surface coverage.⁴

The formation of micelles is marked by a sharp change in several physical properties of the system such as surface tension, turbidity, and conductivity.⁴ This sharp change in properties occurs in a narrow concentration range and can be exploited to indirectly determine the concentration at which micelles begin to form – termed the CMC. The determination of CMC by surface tension measurement is widely reported in literature with surface tension decreasing as surfactant concentration increases up until reaching a plateau.^{3,4}

Further, it has been recognized that micelles are not truly water-soluble and exist as dispersed liquid particles.^{3,4} This property can be used to directly measure CMC values using optical methods based on enhanced fluorescence of marker probes that segregate to the hydrophobic environment of micelle interiors. This type of approach (fluorescence spectroscopy using Nile red (NR) as marker probe) was used by Mackenzie et al. to study micelle formation of a commercial corrosion inhibitor known to include alcohols and active imidazoline-based components.⁵

Prior research conducted by the authors involved integrating experimental methodologies typically used to determine CMC (Surface Tension and Fluorescence Spectroscopy) with methodologies implemented to measure the CMA on platinum (based on capacitance vs potential, cyclic voltammetry and quartz crystal microbalance).^{6,7} Results obtained with homologous series of quaternary amines and imidazolines, which are some of the constituents commonly used in oil and gas corrosion inhibitor formulations, indicated that micellization and adsorption on platinum processes are not only closely related to each other but are also related to CO₂ corrosion inhibition.^{8,9}

A second type of molecule (e.g., heterocyclic aromatic compounds), also used as a constituent of inhibitor formulations, does not behave as a surfactant. Therefore, these molecules cannot be characterized in terms of CMC, but they do show surface activity on Pt and can be characterized in terms of CMA.

Molecules with a pyridine ring (hereafter referred as pyridine-like molecules) have been used as components of commercial inhibitors and are known themselves to be inhibitors.^{10,11} Acridine has been noted to be a potent corrosion inhibitor on carbon steel in crude oil environments.¹² More generally, pyridine, quinoline, and acridine have been reported to be corrosion inhibitors of Fe and steel in 5% HCl solutions at 25°C.¹³ In that study, quinoline was reported primarily to be a cathodic inhibitor, while pyridine was primarily an anodic inhibitor, and acridine showed mixed inhibition, decreasing both anodic and cathodic reaction rates approximately equally.¹³ The degree of inhibition increases with the number of rings (i.e., acridine was the most potent inhibitor).¹³ The authors suggested that the initial adsorption of inhibitor is a cooperative chemisorption process that involves chloride, rather than a competitive process.¹³ Another study indicated that quinoline is an inhibitor in acid environments, although various pyridine and quinoline derivatives may be superior inhibitors.¹⁴

It has been reported that these types of molecules may change the orientation of adsorption depending on concentration. For example, Pyridine adsorption on Ni (111) tends to be planar to the surface (using the aromatic π electrons) at low coverage and change to almost perpendicular (bond involving the Nitrogen atom) at high coverage.¹⁵ For Quinoline on Pd (111), adsorption seems to be almost flat, predominantly from the aromatic π system.¹⁶

For molecules with and without aliphatic chains, there are critical concentrations at which surface coverage or inhibition is maximized and beyond which additional inhibitor does not provide additional

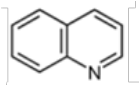
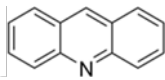
benefit.⁵ Identification of these critical concentrations for different inhibitors and in different environmental conditions has immense value for optimizing corrosion inhibition while also optimizing cost and perhaps maintenance schedules. One of the primary objectives of this and previous research work has been to identify the minimum concentration of inhibitor needed to achieve a maximum surface coverage for a given set of environmental conditions.⁶⁻⁹ The difference in molecular morphology and adsorption mechanism relative to inhibitors with an aliphatic chain and surfactant properties has a direct impact on what experimental techniques are available to characterize the adsorption behavior.

The present work evaluated the effect of critical parameters such as pH, salinity, temperature and number of rings in the molecular structure on the adsorption process of pyridine-like molecules. Adsorption isotherms were determined under different solution conditions and were used to calculate thermodynamic constants – Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) change associated with this process. Additional studies were conducted to understand the effect of protonation on the adsorption properties of these molecules. The correlation between the CMA values obtained in this work and CO₂ corrosion inhibition will be presented in another paper.¹⁷

EXPERIMENTAL METHODOLOGY

The compounds evaluated in this work are shown in Table 1 along with their molecular structures.

Table 1
Molecular Structures of Inhibitors Evaluated

Pyridine	
Quinoline	
Acridine	

Pyridine, quinoline, and acridine pKa values were determined by measuring titration curves of each chemical in 1.0 L of 1% NaCl solution at room temperature. For quinoline and pyridine, the initial solution concentration of inhibitor was 10 mM and a 0.1 N HCl titrant was used. The solubility of acridine in water was relatively low compared to quinoline and pyridine (approximately 215-300 μ M at room temperature and the solubility increases in acids by forming its conjugate acid (acridinium)).¹⁸ The solubility of quinoline at room temperature has been reported to be approximately 40 mM.¹⁹ As a result, a starting concentration of 0.2 mM acridine inhibitor was selected and a 0.01 N HCl titrant was used. The pH was measured after each incremental titrant addition and after pH stabilization had occurred. The pH corresponding to the half-equivalent point was considered equal to the pKa. It was assumed that there was full reaction between HCl and the inhibitor molecules to yield mono-protonated molecules.

The adsorption properties on platinum for different inhibitor molecules at controlled temperatures were studied using capacitance vs potential (MS), cyclic voltammetry (CV), quartz crystal microbalance (QCM) measurements. These measurements were made using the same semi-integrated system and experimental procedure presented in an earlier work by the authors.⁶ The system was designed so that the test solution could be prepared in a pre-conditioning vessel (PCV) before being pumped to different “stations” where the above measurements were performed. This allows inhibitor injections to be made directly into the PCV before the test solution is distributed throughout the system for individual test measurements. After a set of measurements was completed the test solution was returned to the PCV for the next injection.

The test matrix shown in Table 2 was designed with the aim of understanding adsorption behavior of pyridine, quinoline, and acridine compounds individually under different condition of pH (3.5, 5.0, and 6.5), ionic strength (0.1%, 1.0%, and 10.0% NaCl in weight), temperature (30°C, 50°C, and 70°C), as well as comparing behavior across the number of benzene rings in the homologous series of pyridine-like molecules. The pH value of the solutions was adjusted before testing started using HCl. A recirculating temperature bath was used to maintain the test solution temperature.

Table 2
Pyridine, Quinoline, and Acridine CMA Test Matrix

Temperature									
	30°C			50°C			70°C		
	Salinity (% NaCl)								
Nominal pH	0.10%	1%	10%	0.10%	1%	10%	0.10%	1%	10%
Pyridine									
3.5		Test						Test	
5	Test	Test	Test		Test			Test	
6.5		Test						Test	
Quinoline									
3.5		Test			Test			Test	
5	Test	Test	Test		Test			Test	
6.5		Test Test			Test			Test	
Acridine									
3.5	Test	Test	Test		Test			Test	
5	Test	Test	Test	Test	Test	Test	Test	Test	Test
6.5	Test	Test Test	Test		Test			Test	

RESULTS AND DISCUSSION

pKa Determination

To help understand the degree of protonation for pyridine, quinoline, and acridine as a function of pH, titration curves were measured in duplicate and used to determine pKa values. These pKa values were then used to calculate a percent protonation as a function of different pH values. The degree of inhibitor protonation or deprotonation can impact inhibitor interaction/activity on the surface, and as a result the CMA. More surface-active forms of inhibitors are anticipated to require lower overall solution concentrations of inhibitor to slow corrosion rates compared to less surface-active forms.

The pKa values obtained for pyridine, quinoline, and acridine are summarized in Table 3. The pKa value for pyridine was found to be approximately 5.3 to 5.4, while the pKa value for quinoline was found to be approximately 5.0. The pKa values for acridine were measured to be between 5.6 and 5.7. Consequentially, pyridine, quinoline, and acridine are weak acids in water electrolytes. In general, the experimentally determined pKa values were in close agreement, although marginally higher than pKa values obtained from literature. For quinoline, pKa has been shown to increase as the ionic strength of the solution increases.

Table 4 shows the percent protonation at room temperature for each inhibitor, as a function of pH, estimated using equation (1) and the pKa values measured.

$$\text{Protonated Form \%} = \frac{100}{(1 + 10^{pH-pKa})} \quad (1)$$

For pyridine, quinoline, and acridine at room temperature, the molecules are predominately in protonated forms at pH 3.5, while the molecules are in predominately non-protonated forms at pH 6.5. At pH 5.0 the molecules were partially protonated.

Table 3
Summary of pKa values and experimental conditions for pyridine, quinoline, and acridine titration tests in 1.0 L of 1% NaCl solution at room temperature using HCl titrant.

Inhibitor	pKa Values	Initial Inhibitor Concentration	Titant Concentration	Literature pKa Values
Pyridine	5.3 – 5.4	10 mM	0.1 N HCl	5.25 ²⁰
Quinoline	5.0	10 mM	0.1 N HCl	4.85 ²¹ , 5.29 ^{19*}
Acridine	5.6 – 5.7	0.2 mM	0.01 N HCl	5.58 ²²

*Experimentally determined for a 0.16 ionic strength solution

Table 4
Percentage of Pyridine, Quinoline, and Acridine in protonated forms at room temperature based on experimentally determined pKa values.

pH	Pyridine	Quinoline	Acridine
3.5	98.6 %	96.9 %	99.3 %
5.0	68.6 %	50.0 %	82.0 %
6.5	6.5 %	3.1 %	12.6 %

Method for Characterizing Inhibitor Adsorption on Platinum

As previously discussed, three different methodologies were used to measure inhibitor adsorption onto platinum. However, due to space limitations, this paper will only present and discuss results based on adsorption coverage data at one potential, derived from the capacitance vs potential (MS) methodology.

The important mathematical equations are summarized below. Additional information can be obtained in a previous work.⁶

The surface coverage θ of the Pt surface by the surfactant at different potentials was calculated from MS results using equation (2) below:

$$\theta = 1 - Z_o'' / Z_i'' \quad (2)$$

where Z_i'' and Z_o'' are the imaginary component of impedance of the system with and without surfactant, respectively, measured at 1 kHz.

In general, the surface coverage vs potential curves are characteristic of the surfactant under study. As a sample, Figure 1 shows surface coverage data for pyridine on Pt as a function of applied potential for concentrations ranging from 0.065 μ M to 64 μ M.

The surface coverage at selected potentials was plotted against inhibitor concentration to generate adsorption isotherms. A Langmuir adsorption isotherm model, of the form shown in equation (3), was used to fit the obtained surface coverage data from MS method and surfactant concentration (C) data to obtain the equilibrium constant for the adsorption process (K_{ads}) which was in turn used to calculate the Gibbs free energy of adsorption (ΔG_{ads}) through equation (4).

$$C/\theta = C + 1/K_{ads} \quad (3)$$