



## DETERMINATION OF CRITICAL MICELLE CONCENTRATION (CMC) OF CORROSION INHIBITOR VIA ELECTROCHEMICAL MEASUREMENT

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### ABSTRACT

The critical micelle concentration (CMC) of an imidazoline-based corrosion inhibitor in CO<sub>2</sub>-saturated 3% NaCl solution was determined via electrochemical measurements, namely electrochemical impedance spectroscopy and linear polarization resistance. The electrochemical parameters, polarization resistance ( $R_p$ ) and charge transfer resistance ( $R_{ct}$ ), were plotted against the inhibitor concentrations. CMC of the studied inhibitor was determined from the plots, where the slope changed their values. Analysis of the impedance data revealed that the adsorbed inhibitor films had different structures, which were influenced by the concentration of the inhibitor.

**Keywords:** CO<sub>2</sub> corrosion, critical micelle concentration, EIS, imidazoline, surfactant.

### INTRODUCTION

Carbon dioxide (CO<sub>2</sub>) corrosion is one of the predominant forms of attack in oil and gas industry. This is due to the fact that the transportation pipelines, which are mostly made from carbon and low-alloy steel, are very susceptible to corrosion in CO<sub>2</sub>-containing environment. Corrosion inhibitors have been the preferred method to mitigate CO<sub>2</sub> corrosion due to economics and ease of application. They can be introduced in-situ without disrupting the transportation process and they are able to protect the hard-to-reach surfaces inside the pipes [1]. Most of the corrosion inhibitors used are organic nitrogenous compounds such as amines, amides, imidazoline and their derivatives.

Corrosion inhibitors are categorized as surfactant because of their molecular structure, which consists of hydrophilic and hydrophobic parts. Figure-1 shows a typical structure of an organic inhibitor. The hydrophobic non-polar part of the inhibitor molecule consists of hydrocarbon chain ( $R_1$ ), whereas the hydrophilic polar part may be one or several functional groups such as -NH (amine), -SH (mercapto), -OH (hydroxyl), -COOH (carboxyl), -PO (phosphate) or their derivatives [2]. Organic corrosion inhibitors are usually referred to as film-forming inhibitors. The functional groups, which are also known as the anchoring groups, allow the inhibitor molecules to dissolve in water and attach to the steel surface. The hydrocarbon chains interact with each other and form hydrophobic film that partially blocks the active surface area.



**Figure-1.** Molecular structure of organic corrosion inhibitor.

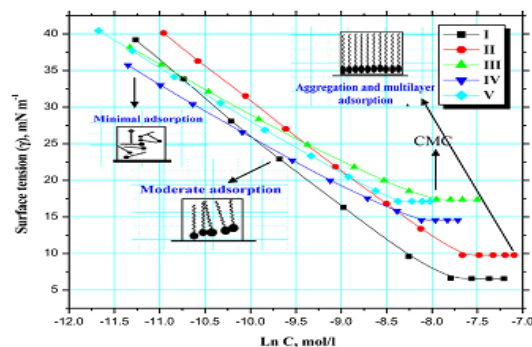
Inhibitor molecules tend to associate with one another into organized molecular assemblies called

micelles. Micellization of the inhibitor molecules occurs once a certain concentration is exceeded. This concentration is known as the critical micelle concentration (CMC). With respect to film formation, CMC is denoted as the boundary condition, below which the surface coverage by the inhibitor molecules is a monolayer or less, and above which the inhibitor molecules form films with multi-layered structure [3]. The efficiency of the corrosion inhibitor is said to be at the optimum level when the inhibitor concentrations approach CMC. This is because at concentration less than CMC, the steel surface is increasingly covered by adsorbed inhibitor molecules at the sub-monolayer to monolayer level. The inhibition efficiency increases rapidly as more and more active sites are being occupied by the inhibitor molecules [4]. Once the CMC is reached, the steel surface is assumed to be almost fully covered by a monolayer, which is already sufficient for significant inhibition. Further increase in concentration would result in formation of multi-layered structures. These additional layers of inhibitor molecules do not contribute much to the protection provided by the monolayer [5]. They only offer additional resistance towards the supply of oxidant and the transport of reaction products, which results in small changes in inhibition efficiency.

CMC of surfactant molecules is determined through the measurement of any micelle influenced physical property as a function of surfactant concentration [6], and the most common one is the surface tension. The relationship between surface tension and surfactant concentration is shown in Figure-2. The point of intersection of the two straight lines is the CMC of the surfactant. Apart from the physical properties, CMC could also be determined from parameters obtained from electrochemical measurements. Zhu and Free [5] measured the corrosion potential ( $E_{corr}$ ) of X65 carbon steel electrode in CO<sub>2</sub>-saturated aqueous solution containing surfactants. It was found that  $E_{corr}$  did not increase much at surfactant concentrations above CMC levels. Fuchs-Godec [8] plotted  $1/i_{corr}$  versus the logarithm of surfactant



concentration. The slope of the plot changed at a certain surfactant concentration, which coincided with the CMC of the studied surfactant. The same correlation was also obtained by the researcher when the polarization resistance ( $R_p$ ) was plotted versus logarithm of surfactant concentration.



**Figure-2.** A plot of surface tension versus  $\ln$  concentration of surfactants [7].

The objective of the present study is to determine the CMC of imidazoline-based corrosion inhibitor in  $\text{CO}_2$ -saturated 3wt% NaCl solution through electrochemical measurements. In addition, the structure of the inhibitor films was studied and discussed.

## METHODS

The electrochemical measurements were carried out in a 1L glass cell with conventional three-electrode configuration, where a stainless steel rod was used as the counter electrode, Ag/AgCl as the reference electrode and API 5L X65 mild steel as the working electrode. The exposed surface area of the working electrode of ca.  $1 \text{ cm}^2$  was polished using silicon carbide abrasive papers up to 600 grit. Later the surface was rinsed with deionized water and degreased using acetone, and finally dried.

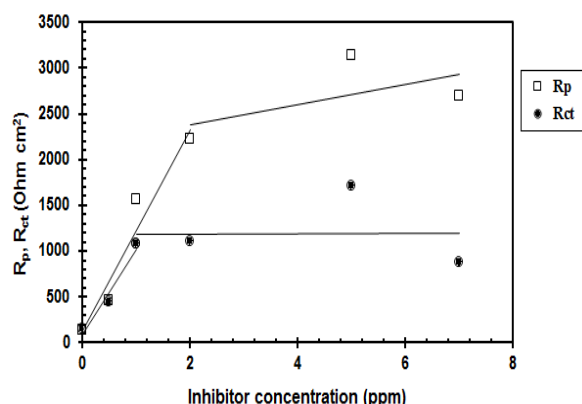
An inhibitor stock solution was prepared by injecting neat inhibitor into 3wt% NaCl solution. The test solutions with different inhibitor concentrations were prepared by diluting the concentrated inhibitor stock solution using 3wt% NaCl solution. Before the commencement of every measurement, test solution was deaerated by purging it with  $\text{CO}_2$  gas at 1 bar for two hours. The purging of  $\text{CO}_2$  gas continued throughout the test in order to minimize air ingress. All tests were conducted at atmospheric pressure and at temperature of  $25^\circ\text{C}$ .

The electrochemical measurements were carried out using a potentiostat (Autolab, Metrohm model PGSTAT128N). Electrochemical impedance spectroscopy (EIS) measurements were performed at open circuit potential, within the frequency range of 10 mHz to 100 kHz and with signal amplitude of 5 mV RMS. The impedance data were analysed with NOVA software (version 1.10.1.9) from Metrohm. Linear polarization resistance (LPR) measurements were made at a potential

range of  $\pm 10 \text{ mV}$  about the corrosion potential and at a scan rate of  $10 \text{ mV/minute}$ .

## RESULTS AND DISCUSSION

In this study, the CMC was determined by plotting electrochemical parameters against inhibitor concentration. The chosen parameters were polarization resistance ( $R_p$ ) and charge transfer resistance ( $R_{ct}$ ), obtained from LPR and EIS measurements respectively. As can be seen in Figure-3, the slopes for both plots changed at certain inhibitor concentrations. It is assumed that the concentrations correspond to the CMC of the studied inhibitor. The values of CMC were determined from the intersection of the two straight lines and the results are listed in Table-1. It is proposed that surface tension measurements should be performed in order to validate this finding.

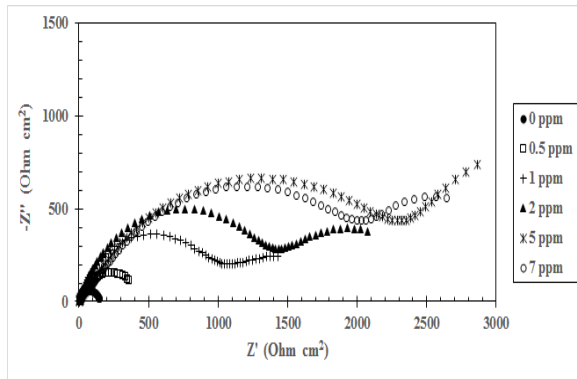


**Figure-1.** Polarization resistance ( $R_p$ ) and charge transfer resistance ( $R_{ct}$ ) as functions of inhibitor concentration.

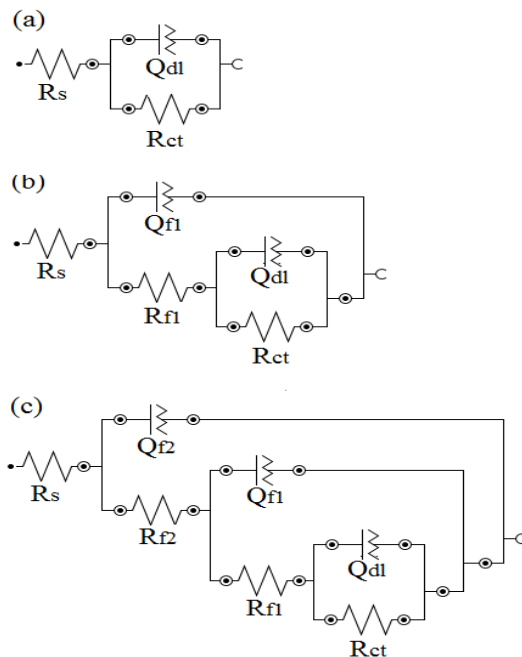
**Table-1.** The values of CMC determined from  $R_p$  and  $R_{ct}$  vs. concentration (c) plots.

Plot	CMC (ppm)
$R_p$ vs. c	2.1
$R_{ct}$ vs. c	1.2

The relatively small changes in both resistance values at concentrations higher than CMC may support the probability that the steel surface was covered by monolayer film and formation of additional layers of inhibitor molecules was probably in progress. The structure of the inhibitor film can be approximately determined through the analysis of the impedance plots. This was done by fitting the impedance plots, as illustrated in Figure-4, to an electrical equivalent circuit model. Examples of common circuit models are shown in Figure-5. The fitted equivalent circuit elements for the impedance plots are listed in Table-2.



**Figure-2.** Impedance plots at various inhibitor concentrations.



**Figure-3.** Equivalent circuit models for: (a) active corroding surface, (b) monolayer inhibitor film, and (c) bilayer inhibitor film.

**Table-2.** Circuit elements of the equivalent circuits for API 5L X65 mild steel in CO<sub>2</sub>-saturated 3wt% NaCl solution with various inhibitor concentrations.

Circuit elements	Inhibitor concentration (ppm)					
	0	0.5	1	2	5	7
$R_{ct}$ ( $\Omega\text{cm}^2$ )	149	446	1076	1103	1705	874
$C_{dl}$ ( $\times 10^{-4}\text{Fcm}^2$ )	4.5	1.9	224	100	174	156
$R_{fi}$ ( $\Omega\text{cm}^2$ )			969	1146	61	99
$C_{fi}$ ( $\times 10^{-4}\text{Fcm}^2$ )			0.5	0.4	0.02	0.03
$R_{f2}$ ( $\Omega\text{cm}^2$ )					2521	2217
$C_{f2}$ ( $\times 10^{-4}\text{Fcm}^2$ )					0.5	0.9

The impedance plots for the blank solution and for the solution with 0.5 ppm inhibitor had the form of a single depressed semicircle. The impedance plot can be fitted to the simple circuit model shown in Figure-5(a). For the blank solution, this means that the electrode was undergoing corrosion process. The corrosion process, represented by double layer capacitor  $Q_{dl}$  and charge transfer resistor  $R_{ct}$ , was charge-transfer controlled. The element  $R_s$  is the resistance of the test solution. The depressed nature of the semicircle was the result of surface roughness and inhomogeneity of the steel electrode [9]. Due to the inhomogeneity of the steel surface, constant phase elements (CPE) are usually used in equivalent circuit models instead of capacitors (C). The impedance of a constant phase element (CPE) is as follows:

$$Z_{CPE} = Y^{-1} (j\omega)^{-n} \quad (1)$$

where  $Y$  is the CPE constant,  $j$  is imaginary unit,  $\omega$  is  $2\pi f$ ,  $f$  is the frequency and  $n$  is the phase shift [10]. The corresponding capacitance value can be calculated using the following equation [11]:

$$C = (Y\Gamma(1-n))^{-1/n} \quad (2)$$

In the case of the solution with 0.5 ppm inhibitor, the value of  $R_{ct}$  increased and this correlates with the enlargement of the diameter of the semicircle. This shows that there was an increase in resistance towards the corrosion process, most probably due to adsorbed inhibitor molecules. It is very common to see impedance plots with two semicircles in the presence of inhibitor, in which one semicircle represents the adsorbed inhibitor film and the other represents the charge transfer process at the metal-solution interface. At 0.5 ppm, the concentration was lower than the previously determined CMC value. Thus the adsorbed inhibitor film may be at sub-monolayer level. The resistance of the inhibitor film may be smaller than  $R_{ct}$  and the semicircle that represents the film was probably merged together with the semicircle of the charge transfer process [10].

At inhibitor concentrations of 1 ppm, the impedance plot can be best fitted to circuit model (b). In this model,  $Q_{fi}$  and  $R_{fi}$  represent the capacitance and resistance of the adsorbed inhibitor film respectively. It can be concluded from the circuit model that a single layer of inhibitor molecules was adsorbed onto the steel surface. This finding supports the value of CMC which was previously determined. Increasing the concentration to 2 ppm increased the magnitude of the impedance but did not change the shape of the impedance plot. At this concentration, the film formed on the surface had the structure of a monolayer but with higher density compared to the film formed at 1 ppm. This is supported by the increased value of  $R_{fi}$  at 2 ppm. On the other hand, the values of capacitance are following a decreasing trend. The equation for capacitance is expressed as:



$$C = \frac{\epsilon \epsilon_0 A}{d} \quad (3)$$

where  $d$  is the thickness of the adsorbed layer,  $\epsilon$  is the dielectric constant of the layer,  $\epsilon_0$  is the permittivity of vacuum and  $A$  is the surface area of the electrode. According to this equation, the decrease in capacitance value could be a result from the decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, which are due to adsorption of inhibitor molecules [7].

At inhibitor concentrations of 5 and 7 ppm, the excellent fitting of the impedance plots to the circuit model (c) revealed that a second inhibitor layer has formed on the steel surface. The second inhibitor layer is represented by  $Q_{12}$  and  $R_{12}$ . However, it was observed that the semicircle at 7 ppm concentration was smaller than that of 5 ppm. The reduction in the size of the semicircle correlates with the decrease in the resistance of the inhibitor film towards the transportation of oxidants and reactants. The possible cause for the decrease in resistance may be related to the repulsion between adsorbed inhibitor molecules [9]. The competition between the inhibitor molecules for adsorption sites may have resulted in less compact and less protective inhibitor film.

## CONCLUSIONS

The followings were concluded from the study:

- The CMC value of the studied inhibitor was determined through electrochemical measurements.
- The measured polarization resistance and charge transfer resistance values increased significantly at concentrations lower than CMC. Once the CMC was surpassed, the changes in their values were relatively small.
- The structure of the inhibitor film depends on the concentration of the inhibitor – sub-monolayer at concentrations below CMC, monolayer at concentrations equal to or greater than CMC, and bilayer at concentrations far greater than CMC.
- Electrochemical impedance spectroscopy is a useful tool for studying inhibition mechanism and analysing inhibitor film structure.

## ACKNOWLEDGEMENTS

Authors would like to acknowledge the university (UTP) and Centre for Corrosion Research. This work was supported by Malaysia government (MyBrain) program for financial support.

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