

Analysis of Corrosion Inhibitor Performance Curves Using Langmuir Adsorption Kinetics

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ABSTRACT

Many corrosion inhibitor performance tests track the corrosion rate over time utilizing electrochemical methods such as linear polarization resistance (LPR). In most of these tests only a portion of the test data gathered are utilized in the final analysis of the corrosion inhibitor performance, namely, the initial uninhibited corrosion rate and the final steady state inhibited corrosion rate, from these two results the corrosion inhibitor performance or efficiency is calculated. Unfortunately, in this approach only the start and end of the test are utilized while the transient response of the corrosion rate versus time curve is discarded. The following paper describes an analysis method using Langmuir adsorption kinetics to extract from the response curve not only the corrosion inhibitor efficiency, but also the adsorption and desorption rate constants.

Key words: Corrosion inhibitor, Performance, Langmuir kinetics, Rate constants

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INTRODUCTION

Often corrosion inhibitor testing involves measuring the corrosion rate prior to the injection of the corrosion inhibitor and then after the corrosion inhibitor is injected tracking the corrosion rate profile in time as the protective corrosion inhibitor film moves toward a steady state condition.

Unfortunately, the analysis of this corrosion inhibitor profile in time is often limited to estimating the uninhibited corrosion rate, C_{Un} , and the final inhibited corrosion rate, C_{In} , at the end points of the test, and the calculation of the corrosion inhibitor efficiency as determined by,

$$C_{Eff} = 1 - \frac{C_{In}}{C_{Un}} \quad (1)$$

As a consequence, much of the data generated at part of the performance-time curve is not utilized in the final analysis of performance. As will be shown later in this paper and in the companion paper, the use of the full data-set can yield significant additional insight into the corrosion inhibitor performance.¹ The limited use of the data generated is illustrated in Figure 3.

LANGMUIR ADSORPTION KINETICS MODEL

Langmuir Kinetic Model

An alternative approach to the analysis of adsorption curves has been presented by Karpovich and Blanchard in 1994 and a more approachable version given in 1995.^{2,3} A very similar kinetic model for adsorption was given in the review article by Azizian.⁴

For the purpose of this paper we will follow the Langmuir kinetic model development of Karpovich and Blanchard. A similar approach has been presented by Ramachandra using a different but clearly related set of equations.⁵

The equilibrium adsorption constant for the Langmuir system is defined as the ratio of the forward and backward rate constants,⁶

$$K_L = \frac{k_a}{k_d} \quad (2)$$

The Langmuir kinetic model of adsorption is given by,^{2,7}

$$\frac{d\theta}{dt} = k_a(1-\theta)C - k_d\theta \quad (3)$$

Where k_a and k_d are the adsorption and desorption rate constants.

It should be noted that at equilibrium, $d\theta/dt = 0$, then Equation (3) reduces to the steady-state/equilibrium isotherm representation often used in corrosion inhibitor assessment, namely,

$$K_L = \frac{k_a}{k_d} = \frac{1}{C} \frac{\theta}{1-\theta} \quad (4)$$

Which in turn can be rearranged to give a further set of familiar relationships,

$$\theta = \frac{K_L C}{1 + K_L C} = CI_{Eff} \quad (5)$$

$$CI_{Eff} = 1 - \frac{CR_{In}}{CR_{Un}} \approx \theta(\infty) \quad (6)$$

Integration of Equation (3) using the initial condition $\theta(t)=0$ at $t=0$ yields the time dependent surface coverage given below,

$$\theta(t) = \frac{C}{C + (k_d/k_a)} \left[1 - \exp(-(k_a C + k_d)t) \right] \quad (7)$$

The result can then be further simplified by substituting $k_{Obs} = k_a C + k_d$ and $K' = C/(C + k_d/k_a)$

$$\theta(t) = K' \left[1 - \exp(-k_{Obs}t) \right] \quad (8)$$

It is this expression which will be used in the analysis of the corrosion inhibitor response curve.

An additional expression which will be used is the steady state surface coverage, as $t \rightarrow \infty$, given by,

$$\theta(\infty) = \frac{C}{C + (k_d/k_a)} = \frac{C}{C + 1/K_L} \quad (9)$$

EXPERIMENTAL PROCEDURE

Rotating Cylinder Electrode

Rotating Cylinder Electrode (RCE) experiments were performed in one liter electrochemical cells as shown in Figure 1. The schematic, also shown in Figure 1, provides the typical components used, which included:

- A Reference Electrode
- B Gas Inlet
- C Gas Outlet
- D Counter Electrode
- E Rotating Shaft
- F Temperature Probe
- G Rotating Cylinder Electrode or Coupon (Working Electrode)

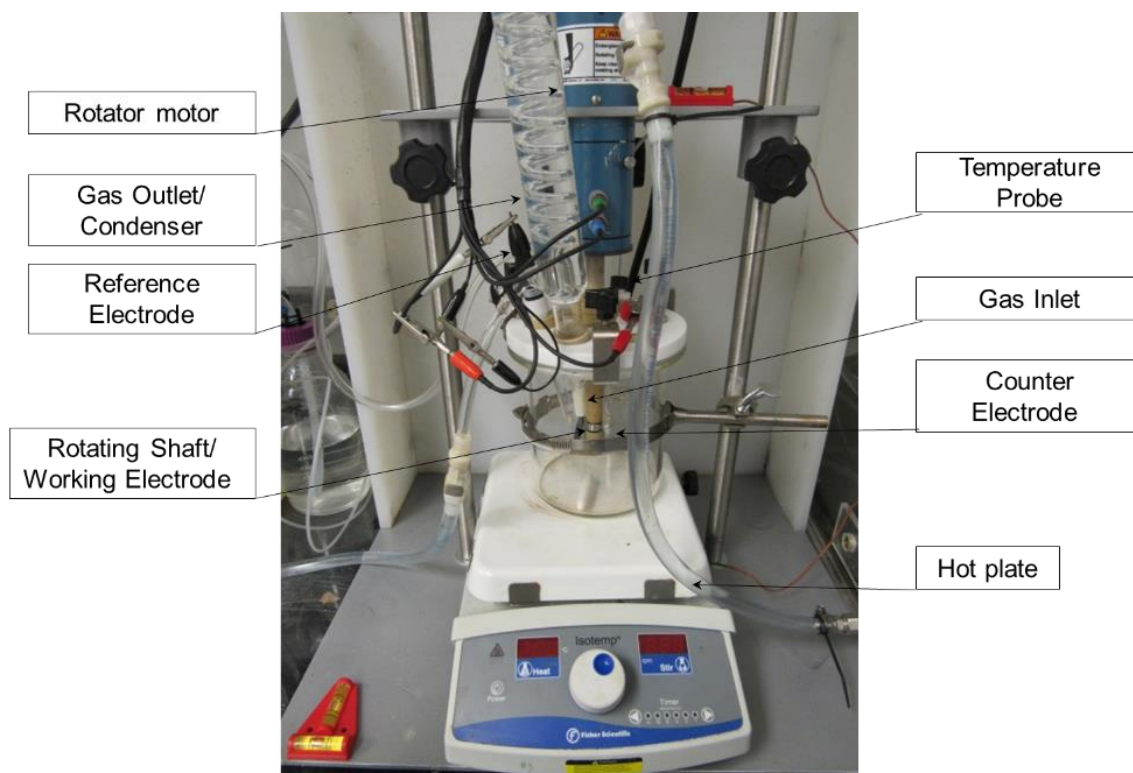


Figure 1: Photograph of the apparatus used with the major components labelled.^{9,10}

A three-electrode configuration was used for electrochemical measurements. The reference electrode was Ag/AgCl and a platinum wire served as the counter electrode. Measurements were performed with a commercial potentiostat. The corrosion rate was determined by Linear Polarization Resistance (LPR), polarizing the electrode ± 10 mV vs OCP at a scan rate of 0.5 mV s^{-1} .¹¹

Synthetic brine was prepared from reagent grade sodium chloride and deionized (DI) water to make up a 5 wt% NaCl solution or approximately 0.8 M. The brine was de-aerated by purging with research grade CO_2 to achieve a dissolved oxygen (DO) concentration less than 10 ppb and pre-heated to test temperature. One liter of the conditioned brine was transferred into the de-aerated electrochemical cell.

A cylindrical sample was machined from carbon steel, with composition provided in Table 1, to the dimensions 15 mm OD and 6.5 mm height (i.e. surface area of 3 cm^2). The steel electrode was polished using SiC paper with 600-grit finish prior to testing. The electrode was degreased by sonication in solvent baths loaded onto the RCE shaft fixture.

The following experimental parameters and constants were used to determine the corrosion rates:

- Equivalent weight of Fe = $55.8/2 = 27.9 \text{ g eq}^{-1}$
- $\rho = 7.87 \text{ g cm}^{-3}$

- $\beta_a = 120 \text{ mV}$
- $\beta_c = 120 \text{ mV}$

Table 1
Composition of stock carbon steel used to machine RCE electrodes.
Values provided in wt%, where the balance is iron (Fe)

C	Si	Mn	P	S	Cu	Ni	Cr
0.07	0.11	1.54	0.008	0.002	0.17	0.18	0.03
Mo	V	Ti	Nb	Al	N	B	
0.01	0.05	0.018	0.035	0.034	0.028	0.001	

Corrosion Inhibitor and Dosage

The corrosion inhibitor used, Inhibitor A, was a commercial product.

Free showed that surfactant aggregation properties of the corrosion inhibitor had a significant impact on performance with the performance plateauing for concentrations above the critical micelle concentration (CMC).¹²

In order to determine the CMC a series of surface tension measurements were conducted and shown in Figure 2.¹³ The CMC was determined to be approximately 100 μM with corrosion inhibitor being dosed at the measured CMC in further corrosion rate testing. The molecular weight was estimated as a weighted average of the active components identified in the manufacturers/supplier data sheet.

RESULTS AND ANALYSIS

The results from the LPR measurements of the corroding electrode are shown in Figure 3 along with the often used analysis of the end points to establish the uninhibited corrosion rate, CR_{Un} , inhibited corrosion rate, CR_{In} , and the corrosion inhibitor efficiency, CI_{Eff} .

As discussed earlier, only a modest amount of the data is utilized in the analysis of the response before and after the addition of the corrosion inhibitor. In this paper we attempt to utilize the “unused” data to gain greater insight into inhibitor performance. The first step in process is to transform the corrosion rate versus time curve into a surface coverage, θ , versus time curve using $\theta = 1 - CR_{In}/CR_{Un}$, the results of this manipulation are shown in Figure 4.