

## Predictability of Corrosion Inhibition Efficiency of Hydroxypropyl Cellulose on Aluminium in Sulphuric Acid

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**Abstract:** Attempt has been made to predict the corrosion inhibition efficiency of hydroxypropyl cellulose (HPC) on aluminium in sulphuric acid. The prediction was carried out within a range of process parameters considered during the experiment. These values are 80.67-95.92 (%), 1-5 (g/l) and 4.03-19.15 ( $\mu\text{Acm}^{-2}$ ) for inhibition efficiencies, inhibitor concentrations and current densities respectively. Evaluation from the process parameters indicates that the corrosion inhibition efficiency of HPC on the aluminium surface is mathematically a function of sum of two parts; the powers of the inhibitor concentration and current density. Derived empirical model;  $\xi = 39.86 \beta^N + 56.69^S + 0.001$  predicts the inhibition efficiency of HPC with maximum deviation < 0.9% (from actual results). This translated into over 99% operational confidence levels for the derived model. The validity of the model was rooted on the core model expression  $\xi - \beta^N = 56.69^S + 0.001$  where both sides of the expression are correspondingly almost equal. The standard error incurred in predicting the model-based inhibition efficiency relative to values of the actual results is 0.42. The correlation coefficients between corrosion rate and reaction temperature, inhibitor concentration and exposure time were all > 0.97.

**Key words:** Aluminum - Corrosion inhibition - Hydroxypropyl cellulose - Sulphuric acid

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### INTRODUCTION

Light alloys such as those of aluminum have found applications in the industries for the production of cooking pots and plates, pipes and fittings, reaction vessels, reaction tanks, storage tanks [1].

Studies [2, 3] have shown that aluminum is susceptible to corrosion attack both in the presence of atmospheric air due its level of passivity and also in acidic environments. Metal corrosion is always observed in industries that do with storage of chemicals, flow of acids solutions and other fluids, just like in the case of cleaning of metallic structures, descaling, electrochemical etching, pickling, etc. [4]. Based on the foregoing, corrosion of metals and its control has become a source of concern in terms of

finding a way for abating failure of steel structures due to corrosion and reducing material loss, saving cost of maintaining steel structural components in the industries and ensuring healthy working environments.

Inhibitors are employed to reduce corrosion attack. These chemicals act as barrier against the aggressive environment which tend to attack the metal surface.

Research [5] has revealed that the polar functional group of a good and reliable inhibitor must possess oxygen, sulphur, nitrogen, cyclic ring or aromatic structure in their molecular or chemical structure [5].

Hydroxypropyl cellulose, having possessed some desirable characteristics, has found application in corrosion inhibition of metal [6]. These characteristics include solubility in water, appreciably safe in handling, and applicability in drilling operations.

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Organic inhibitors have been appraised [7] and found capable of replacing corrosion inhibitors that are acute to human health and environment even though they are effective. This has prompted research and development to produce corrosion inhibitors from polymeric backgrounds to protect metals in destructive service environments.

Report has shown that some corrosion inhibitors of polymer extraction function by retarding the aggressiveness of the corroding environment on the metal surface. These polymers include starch [8-10], carboxymethyl cellulose [11, 12], chitosan [13], gum arabic [14] water-soluble polymers [15], a blend of polyvinylpyrrolidone and polyacrylamide [16], etc.

Scientists have successfully investigated [17] the adsorption and inhibition performance of hydroxypropyl cellulose (HPC) on aluminium corrosion in 0.5 M HCl and 2M H<sub>2</sub>SO<sub>4</sub> at 30-65°C using potentiodynamic polarization, gravimetric measurement and quantum chemical computation technique respectively.

Results of the analysis on potentiodynamic polarization confirmed that HPC acted as a mixed-type inhibitor in both aggressive solutions with a more dominant anodic effect. Aluminium was observed to dissolve with ease in hydrochloric acid compared to sulphuric acid. The inhibition efficiency of HPC increased with increase in inhibitor concentration within a range of increased temperature. It was observed that Langmuir adsorption isotherm play its self out during the adsorption of HPC molecules onto aluminium surface. Furthermore, the adsorption strength attractiveness of HPC molecules towards aluminium surface was revealed by the quantum chemical calculations through the aid density functional theory. It is worthy of note that metal corrosion in acids still exists, despite of the significant contributions of some polymers as corrosion inhibitors for metals in various aggressive media. Furthermore, the effectiveness and durability of polymeric inhibitors vary with metals, corrodents, the condition of corrosion environment, etc. This has raised the need for intensive and extensive research to ascertain the best favourable condition at which the polymeric inhibitors can perform to reduce the metal corrosion to the lowest ebb.

Hydroxypropyl cellulose has been successful used [17] as an effective corrosion inhibitor for aluminium in acidic environments. However, no work has been published, to relate in mathematical terms the process parameters ensuing from the research.

The present research aims at predicting the corrosion inhibition efficiency of hydroxypropyl cellulose on aluminium in sulphuric acid.

## MATERIALS AND METHODS

**Materials Preparation:** The aluminium sheet used for the study has the following chemical composition (wt%): Si (0.842%), Fe (0.898%), Cu (0.028%), Mn (0.081%), Mg (0.026%), Zn (0.010%), Ti (0.0155), Cr (0.0065), Ni (0.003%), V (0.009%) and balance Al. The sheet was press cut mechanically into 4 × 3 × 0.2 cm coupons. The test coupons were polished with fine emery papers 1000 grades to ascertain smooth surface, degreased with acetone, rinsed in distilled water and dried with warm air. The prepared coupons were stored in a desiccator before use for the corrosion test. The acid solutions were prepared with analytical grade (BDH) of H<sub>2</sub>SO<sub>4</sub> and double distilled water. The blank acid solution used for the research was 2M H<sub>2</sub>SO<sub>4</sub>. For the inhibited solution, powdered HPC (product of Sigma Aldrich chemical company) was added to blank acid solutions to obtain concentrations of 1 g/L, 2 g/L, 3 g/L, 4 g/L and 5 g/L respectively. The HPC was used as obtained without any purification [17].

**Potential Dynamic Polarization Measurements:** Advanced electro chemical corrosion equipment (PARC-263 model) was used to conduct the experimental test. The system consists of cylindrical computer glass electrolytic cell display system and power suite software. The electrolytic cell contains three conventional electrodes (counter electrode (graphite rod), reference electrode (saturated calomel electrode) and the working electrode [aluminium coupons coated with epoxy resin and exposing a surface area of 1 cm<sup>2</sup> to the test solution]) and test solution. The electrodes were connected to the electrolytic cell via the lugging capillary of the electrochemical workstation before the equipment was switched on. Open potential circuit steady-state values were allowed for 30 min of immersion before each potentiodynamic polarization measurement was made in unstirred solution and aerated condition maintained at 30 ± 1°C room temperature and in the potential range ± 250 mV versus corrosion potential at a scan rate of 0.333 mV/s. Power suite software was used to extrapolate the polarization data. Each test was repeated in triplicates to verify the reproducibility of the system [17].

**Gravimetric Loss Measurement:** The weight loss measurement was done by complete immersion of aluminium coupons in 200 mL of blank and inhibited solution respectively contained in 300 mL glass beaker kept at 30 ± °C with the aid of a nylon thread, glass rod, and hooks and thermostatic water bath. The aluminium coupons were retrieved after 24 h interval progressively

for 144 h. Also, the temperature variation effect was monitored by equilibrating the beakers at 35-65°C in a thermostatic water bath and the coupons were retrieved at an interval of 8 h. The experiments were conducted in triplicates to confirm reproducibility of results and the average value of the weight [17].

**RESULTS AND DISCUSSION**

Table 1: Variation of inhibition inhibition  $\xi$ , with current density  $\rho$ , and concentration of inhibitor  $\beta$  [17]

( $\xi$ )	( $\rho$ )	( $\beta$ )
80.67	19.15	1
84.74	15.09	2
88.20	11.67	3
92.67	7.23	4
95.92	4.03	5

Computational analysis of the actual results shown in Table 1, gave rise to Table 2 which indicate that;

$$\xi - \bar{A}\rho^{-S} = \bar{H}\beta^N + K \tag{1}$$

Introducing the values of  $\bar{A}$ ,  $\bar{H}$  and K into equation (1) reduces it to;

$$\xi - 56.6\rho^{-S} = 39.86\beta^N + 0.001 \tag{2}$$

$$\xi = 39.86\beta^N + 56.6\rho^{-S} + 0.001 \tag{3}$$

where,

K = 0.001,  $\bar{H}$  = 39.86,  $\bar{A}$  = 56.6, N = 0.1064 and S = 0.1078; equalizing constant (determined using C-NIKBRAN [18])

( $\xi$ ) = Corrosion inhibition efficiency (%)

( $\rho$ ) = Concentration of inhibitor (g/l)

( $\beta$ ) = Current density,  $i_{corr}$  ( $\mu\text{Acm}^{-2}$ )

**Boundary and Initial Conditions:** Consider short cylindrically shaped aluminium coupon submerged in sulphuric acid, interacting with some corrosion-induced agents. The solution is assumed to be affected by undesirable dissolved gases. The considered range of the inhibition efficiencies, inhibitor concentrations and current densities are 80.67- 95.92 (%), 1- 5 (g/l) and 4.03-19.15 ( $\mu\text{A cm}^{-2}$ ) respectively.

Table 2: Variation of  $\xi - \bar{A}\rho^{-S}$  with  $\bar{H}\beta^N + 0.001$

$\xi - \bar{A}\rho^{-S}$	$\bar{H}\beta^N + 0.001$
39.50	39.861
42.50	42.911
44.77	44.801
46.94	46.201
47.22	47.311

**Model Validity:** The validity of the model is strongly rooted on the core model equation (1) where both sides of the equation are correspondingly almost equal. Table 2 also agrees with equation (1) following the values of  $\xi - \bar{A}\rho^{-S}$  and  $\bar{H}\beta^N + 0.001$  evaluated from the actual results in Table 1. Furthermore, the derived model was validated by comparing the corrosion rate predicted by the model and that obtained from the experiment. This was done using various analytical techniques which includes statistical, graphical and deviational analyses.

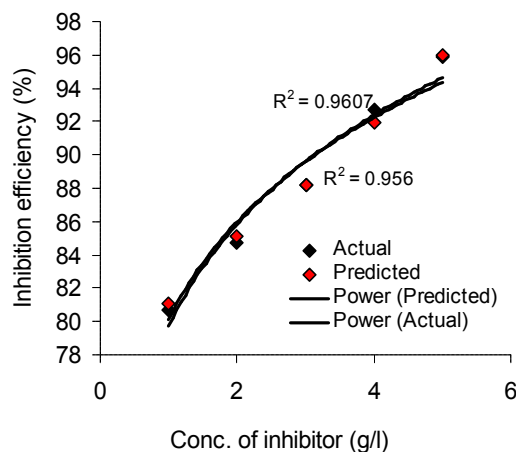


Fig.1: Coefficient of determination between inhibition efficiency and concentration of inhibitor as obtained from actual and model-predicted results

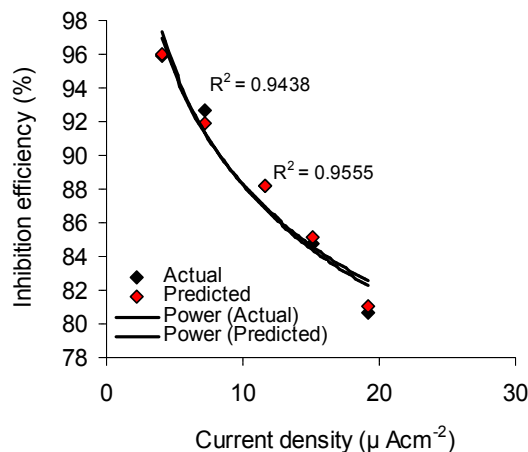


Fig.2: Coefficient of determination between inhibition efficiency and current density as obtained from actual and model-predicted results

**Statistical Analysis**

**Correlation:** The correlation coefficient between inhibition efficiency and inhibitor concentration & current density were evaluated (using Microsoft Excel Version 2003) from results of the actual and derived model. These results are

0.9802 and 0.9778 & 0.9715 and 0.9775 respectively. The evaluations were based on the coefficients of determination  $R^2$  shown in Figs. 1 and 2, and then calculated using equation (4).

$$R = \sqrt{R^2} \quad (4)$$

**Standard Error (STEYX):** The standard error incurred in predicting the model-based inhibition efficiency relative to values of the actual results is 0.42%. The standard error was evaluated using Microsoft Excel version 2003.

**Graphical Analysis:** The validity of the derived model was further verified by plotting values of the actual, besides the model-predicted results using Microsoft Excel (version 2003) to evaluate the trend of both results. Comparative Analysis of Figs. 4 and 5 indicate very close alignment of curves which depicted significantly similar trend of data point's distribution for the actual and derived model-predicted inhibition efficiency. This shows proximate agreement between both results.

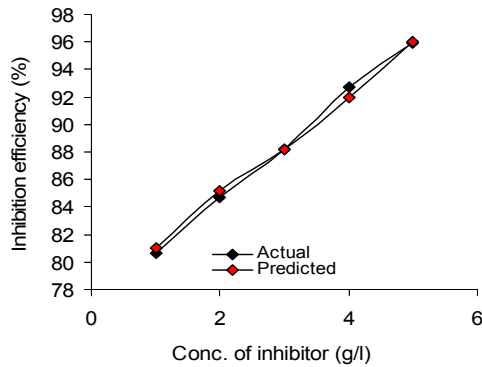


Fig. 3: Variation of inhibition efficiencies with concentration of inhibitor as obtained from actual and model-predicted results

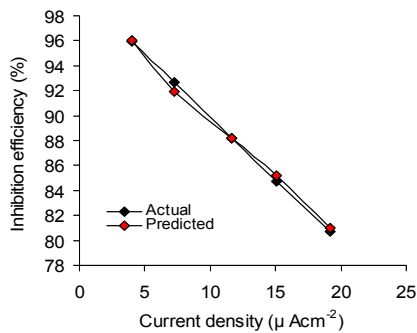


Fig. 4: Variation of inhibition efficiencies with current density as obtained from actual and model-predicted results

**Deviational Analysis:** Analysis of the inhibition efficiency obtained from the actual and model-predicted results shows deviation on the part of model-predicted results. This was attributed to the fact that the effects of the surface properties of the aluminium which played vital roles during corrosion in sulphuric acid were not considered during the model formulation. This necessitated the introduction of correction factor, to bring the model-predicted inhibition efficiency to those of the corresponding experimental values.

The deviation  $Dv$ , of model-predicted inhibition efficiency from the corresponding actual result was given by;

$$Dv = \left( \frac{\xi_P - \xi_E}{\xi_E} \right) \times 100 \quad (5)$$

where

$\xi_E$  and  $\xi_P$  are inhibition efficiencies evaluated from actual and model-predicted respectively'

Fig.5 shows that maximum deviation of model-predicted inhibition efficiency from the actual results was less than 0.9%. This translates into over 99% model operational confidence. The figure shows that the least and highest deviations of model-predicted results (from actual results) are -0.03 and -0.8 %.

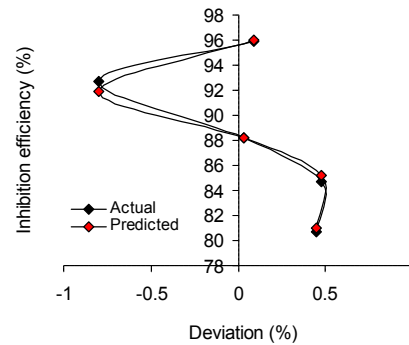


Fig. 5: Deviation of model-predicted results from actual values

These deviations correspond to model-predicted inhibition efficiencies: 88.23 and 91.93 (%); inhibitor concentrations: 3 and 4(g/l) and current densities: 11.67 and 7.23 ( $\mu\text{Acm}^{-2}$ ) respectively.

Correction factor,  $Cf$  to the model-predicted results was given by;

$$Cf = - \left( \frac{\xi_P - \xi_E}{\xi_E} \right) \times 100 \quad (6)$$

Critical analysis of Fig. 5 and Fig. 6 show that the evaluated correction factors are negative of the deviation as shown in equations (5) and (6).

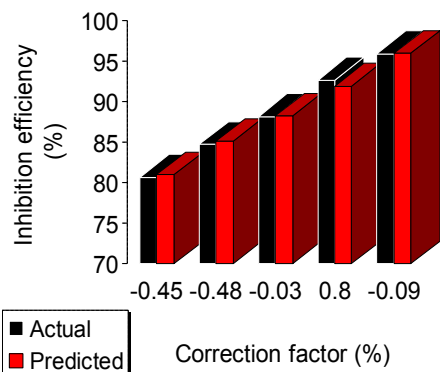


Fig. 6: Correction factor to model-predicted results

The correction factor took care of the negligence of operational contributions of the effects of surface properties of the aluminium which actually affected the corrosion process. Introduction of the corresponding values of Cf from equation (6) into the model gives exactly the corresponding actual inhibition efficiency. Fig. 6 indicates that the maximum correction factor to the model-predicted inhibition efficiency was less than 0.9%. The figure shows that the least and highest correction factors to the model-predicted results (from actual results) are - 0.03 and 0.8%. These correction factors also correspond to model-predicted inhibition efficiencies: 88.23 and 91.93 (%); inhibitor concentrations: 3 and 4 (g/l) and current densities: 11.67 and 7.23 ( $\mu\text{Acm}^{-2}$ ) respectively.

The deviation of model predicted results from that of the actual is just the magnitude of the value. The associated sign preceding the value signifies deviation/deficit (negative sign) or surplus (positive sign).

## CONCLUSION

The corrosion inhibition efficiency of hydroxypropyl cellulose (HPC) on aluminium in sulphuric acid was predicted within a range of process parameters 80.67-95.92 (%), 1-5 (g/l) and 4.03-19.15 ( $\mu\text{Acm}^{-2}$ ) for inhibition efficiencies, inhibitor concentrations and current densities respectively. The corrosion inhibition efficiency of HPC on the aluminium surface is mathematically a function of sum of two parts; the powers of the inhibitor concentration and current density. The derived empirical model;  $\xi = 39.86 \beta^N + 56.69^S + 0.001$  predicted the inhibition efficiency of HPC with maximum deviation < 0.9%

(from actual results). This translated into over 99% operational confidence levels for the derived model. The validity of the model was rooted on the core model expression  $\xi - \bar{A}9^S = \bar{H}\beta^N + 0.001$  where both sides of the expression are correspondingly almost equal. The standard error incurred in predicting the model-based inhibition efficiency relative to values of the actual results is 0.42. The correlation coefficients between corrosion rate and reaction temperature, inhibitor concentration and exposure time were all > 0.97.

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