



# Inhibition Effect of Butan-1-Ol on the Pitting Corrosion of Austenitic Stainless Steel (Type 304)

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## ABSTRACT

The performance of Butan-1-ol (BTU) on the pitting corrosion inhibition of austenitic stainless steel (Type 304) in dilute sulphuric acid contaminated with recrystallized sodium chloride was investigated with the aid of potentiodynamic polarization technique. Corrosion potential, pitting potential, passivation potential, nucleation resistance, passivation range, passivation capacity measurements and potentiodynamic analysis were used to assess the pitting resistance characteristics of the stainless steel. Results showed that pitting potential increased progressively with proportionate increase in BTU concentration. This occurred with corresponding increase in the passivation range which shows an enhanced resistance to pitting corrosion..

**Key Words:** *Corrosion, pitting, sulphuric acid, steel; inhibitor.*

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## 1. INTRODUCTION

Austenitic stainless steel is one of the most versatile metals for applications in buildings as construction material and in various harsh conditions such as in chemical industries, desalination and waste water treatment plants, petroleum industry and metal extraction industries due to its resistance to general corrosion, high

temperature mechanical properties, good fabricability and weldability. The corrosion resistance property is basically due to the passive film formed instantaneously on the steels and has been intensively studied using different surface analysis techniques [1-4]. A chemical combination of iron and chromium oxides formed, with hydroxide and H<sub>2</sub>O concentrated at the outermost region

of the film constitutes the passive film [5-7]. Exposure of austenitic stainless in corrosive aqueous solution causes chromium oxides to enrich at the metal/film interface resulting in the passive layer, which is responsible for its excellent corrosion properties [8-11]. In the presence of aggressive ions, such as chloride anion in seawater, mineral acids etc. local breakdown of passivity occurs, mainly at regions of local heterogeneities, inclusions and impurities causing pitting corrosion.

Pitting corrosion is a localized electrochemical dissolution process which in most cases causes catastrophic failure of passive metals. In this form of corrosion only small areas of the metal surface undergo localized attack, rapidly penetrating into the metal whilst the rest of the surface remains largely unaffected and probably passive [12, 13]. The pitting corrosion resistance of austenitic stainless steels depends on their chemical composition and metallurgical microstructure. Pits location on passive metals is often unpredictable being randomly dispersed on the metal surface especially at non-metallic inclusions [14-17]. Passivity breakdown is followed by pit nucleation, growth, and sometimes repassivation on highly resistant metals [18, 19]. When the rate of passivation is lower than the rate of film destruction, the film does not recover sufficiently and the microscopically formed pit continues to grow consequentially leading to an active macroscopic pit. The consequential process occurs in three steps: nucleation, metastable pit propagation and stable pit propagation [20-23].

A number of organic compounds have been used in the inhibition of general metallic corrosion [24-27]; however the application of organic inhibitors for pitting corrosion inhibition of stainless steels is limited. Pitting corrosion is a complicated localized corrosion phenomenon and the relationship between adsorption of organic compounds and corrosion inhibition applicable in general corrosion is not obvious. This research aims to investigate the inhibition effect of butan-1-ol, and organic compound on pitting corrosion of austenitic stainless steel (Type 304) in dilute sulphuric acid. Butan-1-ol (BTU) is a primary alcohol which occurs naturally as a minor product of the fermentation of sugars and other carbohydrates [28-33]. The largest use of butan-1-ol is as an industrial intermediate, particularly for the manufacture of butyl acetate.

## 2. EXPERIMENTAL METHODS

### Material

Commercially available Type 304 austenitic stainless steel (ASS) was used for all experiments. Analysis from the Applied Microscopy and Triboelectrochemical Research Laboratory, Department of Chemical and Metallurgical Engineering, Tshwane University of Technology, South Africa with average nominal composition of 18.11% Cr, 8.32% Ni and 68.32% Fe. The material is cylindrical with a diameter of 18 mm.

### Inhibitor

Butan-1-ol (BTU) a brownish, translucent liquid is the inhibitor used. The structural formula of BTU is shown in

Fig. 1. The molecular formula is  $C_4H_9OH$  while the molar mass is 74.122 g/mol.

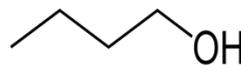


Figure. 1 Chemical structure of Butan-1-ol (BTU)

BTU was applied in concentrations of 2.5%, 5%, 7.5%, 10%, 12.5% and 15% per 200ml of 3 M  $H_2SO_4$  solutions respectively.

### Test Media

3M  $H_2SO_4$  acid with 3.5% recrystallized sodium chloride of analar grade was used as the corrosion test media.

### Preparation of Test Specimens

The cylindrical stainless steel (18 mm dia.) was mechanically cut into a number of test specimens of dimensions in length ranging from 17.8 mm and 18.8 mm coupons. The two surface ends of each of the specimen were ground with silicon carbide abrasive papers of 80, 120, 220, 800 and 1000 grits. They were then polished with 6  $\mu m$  to 1  $\mu m$  diamond paste, washed with distilled water, rinsed with acetone, dried and stored in a desiccator for linear polarization test.

### Linear Polarization Resistance

Linear polarization measurements were carried out using, a cylindrical coupon embedded in resin plastic mounts with exposed surface of 254 mm<sup>2</sup>. The electrode was metallographically prepared with specific grades of silicon carbide paper, polished to 6 $\mu m$ , rinsed by distilled water and dried with acetone. The studies were performed at ambient temperature of 25 °C with Autolab PGSTAT 30 ECO CHIMIE potentiostat and electrode cell containing 200 ml of electrolyte, with and without BTU inhibitor. A graphite rod was used as the auxiliary electrode and silver chloride electrode (Ag/AgCl) was used as the reference electrode. The steady state open circuit potential (OCP) was noted. The potentiodynamic studies were made from -1.5V versus OCP to +1.5 V versus OCP at a scan rate of 0.00166V/s and the corrosion currents were registered. The corrosion current density ( $I_{cr}$ ) and corrosion potential ( $E_{cr}$ ) were determined by the intersection of the extrapolated anodic and cathodic Tafel lines. The pitting potential  $E_{pit}$ , and passivation potential  $E_{pp}$ , were determined from the polarization curve.

## 3. RESULTS AND DISCUSSION

### Nucleation resistance, passivation capacity, passivation range and passivation potential

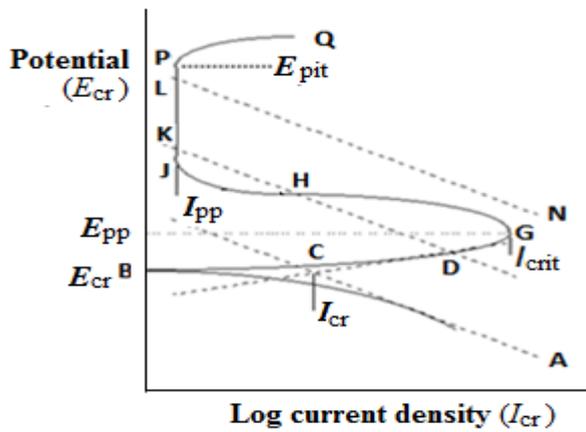
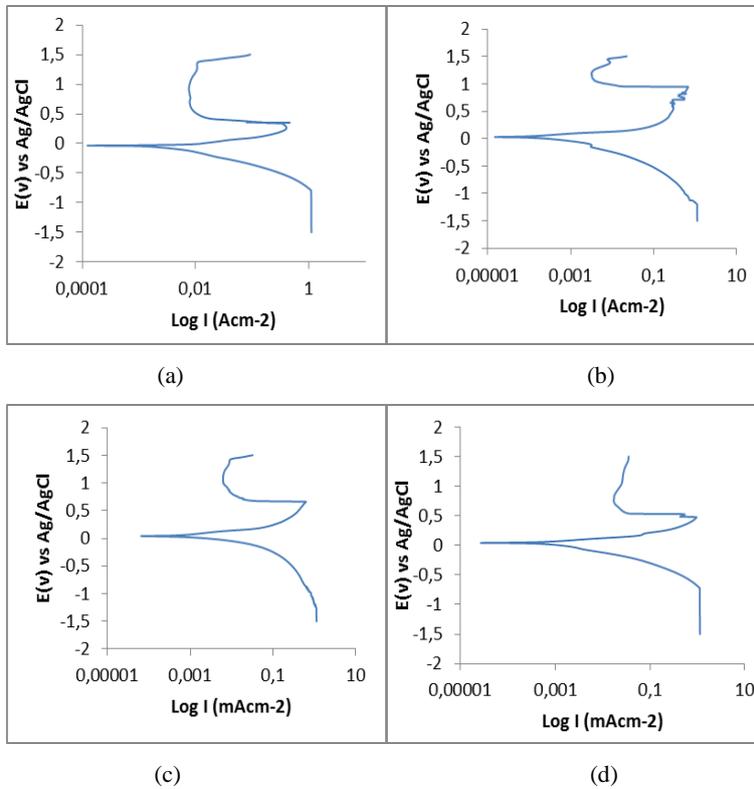


Figure 2. Schematic potentiodynamic polarization behaviour of passivating metals

Figure 2 is a representative polarization plot of the variation of corrosion potential ( $E_{cr}$ ) with the log of current density ( $I_{cr}$ ) for the stainless steel in dilute sulphuric acid /chloride media.

- AB represents cathodic reaction.
- BG represents anodic dissolution reaction. The metal is not passivated at the corrosion potential ( $E_{cr}$ , B).

- AC and DC are Tafel straight lines
- At potentials more positive than B, corrosion rate increases, and reaches a maximum at the passivation potential/ critical current  $I_{crit}$  at point G, which is given the symbol,  $E_{pp}$ .
- The transition from active dissolution occurs in the region G to J. A protective film begins to form and causes a sudden drop in corrosion current density.
- From J to P, the passive zone, the current density is maintained until point P.
- At P (pitting potential  $E_{pit}$ ), breakdown of the protective film begins. It is here that the likelihood of pitting is greatest, and consequently specimen failure.
- $E_{pit}$  often called the critical pitting or breakdown potential is a useful parameter in assessing pitting corrosion properties of materials.



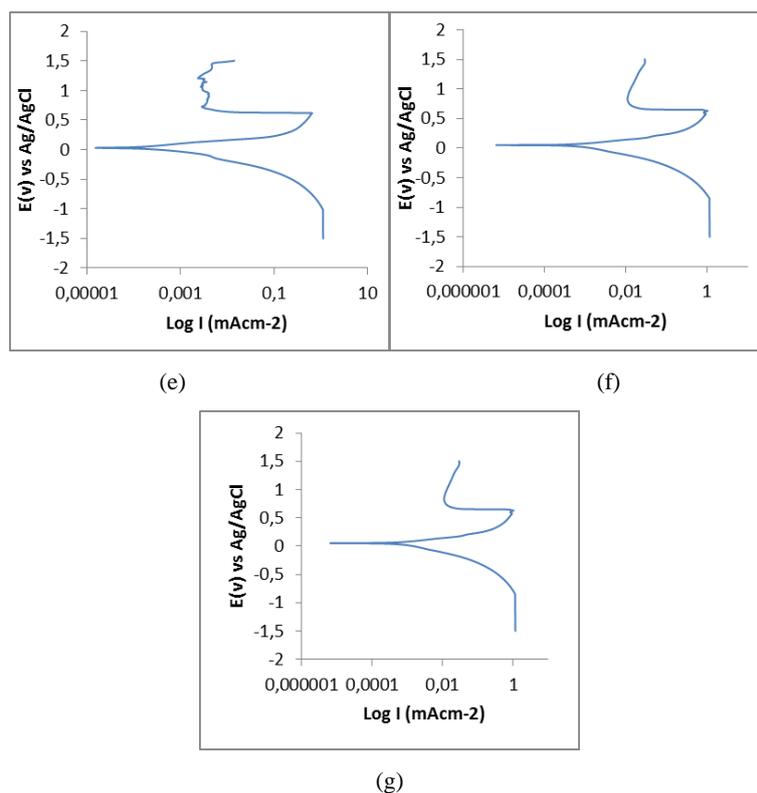


Figure. 3(a-g): Polarization scans for austenitic stainless steel in 3M H<sub>2</sub>SO<sub>4</sub> solution at (0-15%) BTU concentration

Table 1. Potentiostatic values of austenitic stainless steel in 3M H<sub>2</sub>SO<sub>4</sub>/ BTU

Sample	BTU Concentration (%)	Pitting Potential, $E_{pit}$ (V)	Passivation Potential (V)	Passivation Range (V)	Nucleation Resistance (V)	Passivation Capacity (V)	Corrosion Potential, $E_{cr}$ 'Cal' (V)
A	0%	1.258	0.663	0.596	1.294	0.699	-0.036
B	2.5%	1.381	1.054	0.326	1.353	1.026	0.028
C	5%	1.395	0.804	0.591	1.358	0.766	0.037
D	7.5%	1.371	0.699	0.671	1.334	0.662	0.037
E	10%	1.367	0.695	0.672	1.334	0.662	0.033
F	12.5%	1.449	0.685	0.763	1.402	0.638	0.047
G	15%	1.449	0.679	0.770	1.402	0.632	0.047

The polarization scans for austenitic stainless steel in 3M H<sub>2</sub>SO<sub>4</sub> solution at (0-15%) BTU concentrations are shown in Figure 3(a-g). The effects of BTU at the stated concentrations are significant on the potentiostatic parameters ( $E_{pit}$ ,  $E_{cr}$  and  $E_{pp}$ ) shown in Table 1 and hence the pitting resistance of the stainless steel. The pit nucleation resistance NR ( $E_{pit} - E_{cr}$ ), passivation range ( $E_{pit} - E_{rep}$ ) and repassivation capacity RC ( $E_{rep} - E_{cr}$ ) can be considered to be a measure of the susceptibility of alloys to pitting corrosion [34-38]. Alloys exhibiting higher values of nucleation resistance and lower values of repassivation capacity are more resistant to pitting corrosion. The values of NR and RC are shown in Table 1. Nucleation occurrence is due of the creation and

evolution of metastable pits. This pits forms and develops for short period before repassivation at potentials well below the pitting potential and during the induction time before the onset of stable pitting at potentials above the pitting potential [39-40]. The nucleation phase of pitting corrosion entails the collapse of the protective passive film, presence of localised gradients responsible for pit propagation. The pitting corrosion mechanism has been the subject of serious debate for quite a while [41-46]. Transition from nucleating to pit propagating is subject to the fact that within chloride media, the solution within the pit hole becomes very corrosive and highly concentrated with chloride ions resulting in metal dissolution instead of the steel passivating. The chloride ions transport into

the active corrosion regions of the steel to counteract the excessive amounts of metallic ions. This causes increased acidity due to the highly concentrated chloride solution which has an average ionic activity coefficient higher than one. There are also concentration and potential gradients responsible for the migration of metal ions to the pit exterior. A pit will only initiate if the rate of metal dissolution is greater than the rate of passivation in order to sustain the pit acidity that will maintain the dissolution.

#### Influence of BTU on the Pitting Corrosion Evaluation of ASS in 3 M H<sub>2</sub>SO<sub>4</sub>

Severe active general corrosion reactions of anodic dissolution of ASS alloy occurred in the presence of the corrosive anions, (Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>), in all BTU concentrations at high potentials due to pitting failure. Detailed observation of Fig. 3(b-d) shows that increase in BTU concentration has a limited influence on the polarization curve. Corrosion failure occurs almost instantaneously at the pitting potential as a result of the inability of BTU to sustain its protective film most probably due to the weak van der Waals forces responsible for its bonding to the steel surface. This is further confirmed from the low inhibition efficiencies results obtained until 12.5% - 15% BTU concentration where the inhibition efficiency is high.

At these concentrations (12.5% - 15%) transpassivity is totally absent, but its overall influence is negligible. The pitting potential values ( $E_{pit}$ , Table 1), increased with increasing BTU concentration from sample A to G, an indication of the ability of BTU to delay the formation of pits after 0% BTU concentration. Fig. 4 shows the plot of  $E_{pit}$  versus BTU concentration. The  $E_{pit}$  illustrate the inhibitive performance of BTU in pit formation. Pitting occurred at potentials slightly above the values obtained for 0% BTU. The passivation range showed a relative increase consistent with the increase in passivity of the steel as the concentration of BTU increases. The potential at which ASS re-passivates reduces progressively with increase in BTU concentrations, with the exception of sample B where there was a sharp increase in the re-passivation potential due to BTU desorption at this particular concentration. For the remaining samples the re-passivating potential values shows the capacity of BTU to enhance the steels passivation characteristics against corrosion, but the overall impact on the general corrosion rate is negligible until 12.5% - 15% BTU concentration where the inhibition efficiency was significantly high. The decrease in RC coincides with increase in nucleation resistance.

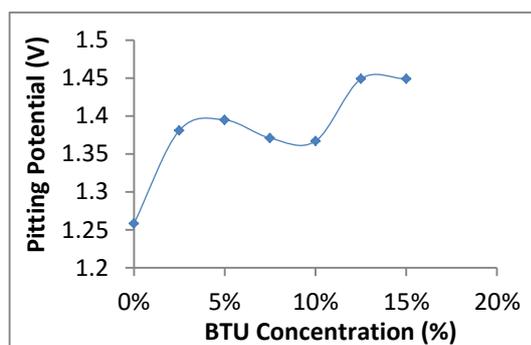


Figure.4 Plot of  $E_{pit}$  versus BTU Concentration

#### 4. CONCLUSION

Potentiodynamic polarization tests, on austenitic stainless steel samples in dilute sulphuric acid contaminated with sodium chloride in the presence of butan-1-ol (BTU) inhibiting compound show that the pitting potential ( $E_{pit}$ ), of the steel increased with increase in BTU concentration. The values obtained from nucleation resistance, passivation capacity and passivation range from the polarization plot at all concentrations of BTU studied showed the significant of BTU on the increased pitting corrosion resistance of austenitic stainless steel.

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#### CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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