Effect of benzotriazole on electrochemical and corrosion behaviour of type 304 stainless steel in 2M sulphuric acid solution

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The effect of benzotriazole ($C_6H_3N_5$) as a corrosion inhibitor for type 304 stainless steel in 2M H_2SO_4 has been studied using weight loss experiments, anodic and cathodic potentiostatic measurements, atomic emission spectrometry, and optical and scanning electron microscopy. Benzotriazole acted as a corrosion inhibitor over the entire range of potentials studied, from −625 to +1250 mV with respect to a saturated calomel electrode, and did not promote selective alloy dissolution. The protective film was stable and adherent and obeyed the Langmuir isotherm, while values of the equilibrium adsorption constant suggested chemical adsorption. The maximum coverage obtained was 0·97 for stirred solutions and 1·0 for unstirred solutions, these values being associated with partial dissolution and lack of dissolution of inclusions respectively.

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INTRODUCTION

Adsorption corrosion inhibitors are used more frequently in acid pickling baths and industrial cleaning equipment because the inhibitive film formed on the metallic surface can completely prevent corrosion. Organic adsorption inhibitors are effective because of their functional group containing heteroatoms such as nitrogen or sulphur. Benzotriazole ($C_6N_3H_5$) has been known to be a corrosion inhibitor for copper and copper alloys for many years[1–4] and more recently has been studied as an inhibitor for iron,[5] cast iron,[6,7] carbon steel,[8] and type 347 stainless steel (SS).[9]

The present paper reports on a study of the inhibitive effect of benzotriazole on the corrosion of type 304 SS in 2M H_2SO_4 solution. Weight loss experiments, anodic and cathodic potentiostatic studies, atomic emission spectrometry, optical microscopy, and scanning electron microscopy (SEM) were used.

EXPERIMENTAL

The chemical composition of the type 304 stainless steel studied was Fe–0·075C–0·47Si–1·28Mn–17·99Cr–0·07Mo–8·00Ni–0·11Co–0·04V–0·05W, where the amount of tungsten is a maximum. Rectangular foils of area 20 cm^2 were used in weight loss experiments and optical analysis. An electrode with a 2 cm^2 working area was used in potentiostatic measurements. The electrodes were abraded successively with 300, 400, and 600 grit emery papers for both weight loss experiments and potentiostatic studies. In the case of micrographic analysis the surface treatment consisted of the same procedure followed by polishing with diamond paste from a surface roughness of 6 μm to a roughness of 1 μm. The cell, with a volume of 1 L, contained a Luggin capillary, a saturated calomel electrode (SCE) as reference, and a large area platinum foil as auxiliary electrode. The solutions were prepared with analytical grade reagents and doubly distilled water. Each experiment used a newly polished electrode and a fresh portion of the solution. Weight loss experiments were carried out with and without use of a magnetic stirrer.

A Carl Zeiss Jena microscope and a Philips model XL 30 scanning electron microscope were used in the microscopic analyses. Potentiostatic measurements were made using an Aardvark Instruments model PEC 1 potentiostat. Inductively coupled plasma atomic emission spectrometry analyses were made using a Spectroflame sequential spectrometer from Spectro.

All experiments were carried out at a room temperature of 27 ± 2°C.

RESULTS AND DISCUSSION

Preliminary weight loss experiments were carried out to verify the absence or presence of selective alloy dissolution. Table 1 gives the results obtained from atomic emission analysis of the solution after immersion of type 304 SS specimens in 2M H_2SO_4 in the absence and presence of benzotriazole. A comparison of these values with the initial composition of the SS shows that selective alloy dissolution was not observed within the experimental error of 5%.

Table 2 gives the values of coverage θ for different benzotriazole concentrations, in stirred and unstirred 2M H_2SO_4 solutions, obtained from the equation

$$\theta = (v_0 - v_i)/v_0$$

where v_0 and v_i represent the corrosion rate in the absence and presence of benzotriazole respectively.

Weight loss experiments showed the effective action of benzotriazole as a corrosion inhibitor for type 304 SS in H_2SO_4 solution. The results correspond to the Langmuir model isotherm, according to the equation

$$C_i/\theta = (1/K_{ads}) + C_i$$

where C_i is the concentration of benzotriazole and K_{ads} represents the adsorption equilibrium constant.

Table 1 Atomic emission analysis of corrosion products for type 304 SS immersed in 2M H_2SO_4 solution with and without benzotriazole for 1 h

Concentration of benzotriazole, mol L^{-1}	Content, wt-%			
	Fe	Mn	Cr	Ni
0	70·0 ± 1·0	1·50 ± 0·2	20·0 ± 1·0	8·8 ± 0·5
$6·5 \times 10^{-6}$	71·0 ± 1·0	1·50 ± 0·2	19·0 ± 1·0	8·2 ± 0·5

a b c

a after polishing, ×1502; *b* after immersion in stirred 2M H_2SO_4 solution without benzotriazole, ×1495; *c* after immersion in stirred 2M H_2SO_4 solution containing $1{\cdot}0 \times 10^{-3}$M benzotriazole, ×1510

1 *Scanning electron micrographs of type 304 SS*

Values of K_{ads} were found to be $6{\cdot}0 \times 10^5$ and $2{\cdot}38 \times 10^5$ mol^{-1} L in the stirred and unstirred systems respectively. These K_{ads} values correspond to chemical adsorption similar to that observed for copper[10,11] and brass[12] in H_2SO_4 solutions.

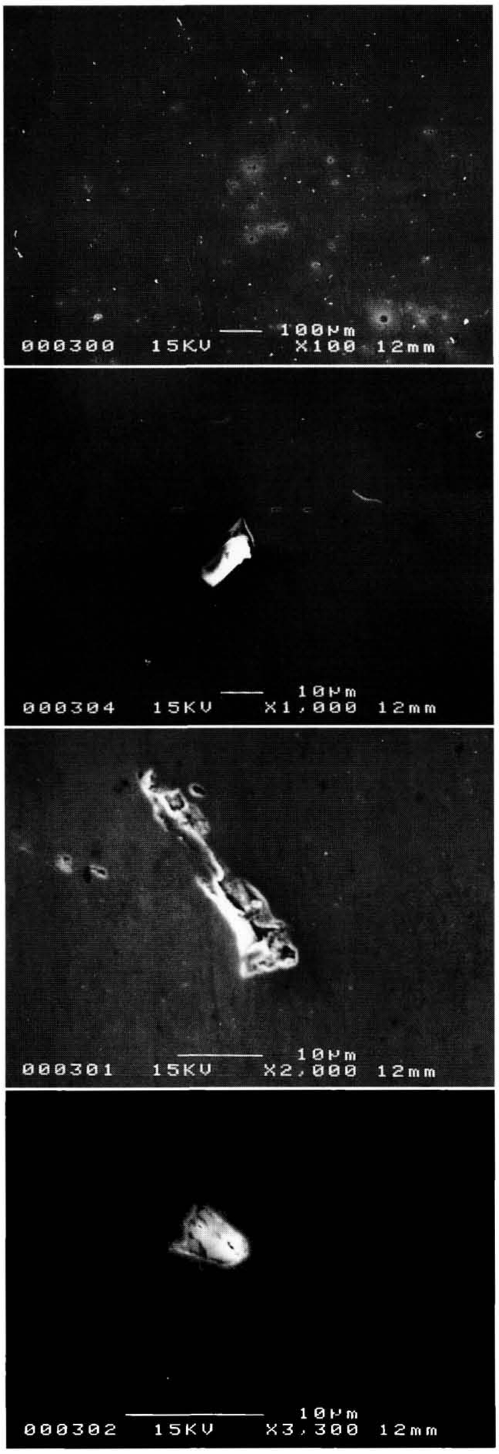
The maximum coverage θ_{max} values obtained were 0·97 and 1·0 with $C_i > 1{\cdot}0 \times 10^{-3}$ mol L^{-1} for stirred and unstirred solutions respectively. Figures 1 and 2 show results of SEM analyses for a type 304 SS surface. Figure 1*a* shows a characteristic inclusion observed on the polished surface, which was probably an oxide inclusion.[13] Figure 1*b* shows the complete dissolution of inclusions when the specimen was immersed in 2M H_2SO_4 solution without benzotriazole. Figure 1*c*, however, indicates that in the presence of benzotriazole in stirred solutions the inclusions are partially dissolved.

Atomic emission spectrometry analysis of 2M H_2SO_4 solutions containing $1{\cdot}0 \times 10^{-3}$M benzotriazole, after immersion of type 304 SS for 1 h, showed an iron

Table 2 Degree of coverage θ of type 304 SS immersed in stirred and unstirred 2M H_2SO_4 solutions containing different concentrations of benzotriazole for 1 h

Concentration of benzotriazole, mol L^{-1}	θ Stirred	θ Unstirred
$6{\cdot}5 \times 10^{-6}$	$0{\cdot}36 \pm 0{\cdot}02$	$0{\cdot}31 \pm 0{\cdot}02$
$9{\cdot}5 \times 10^{-6}$	$0{\cdot}45 \pm 0{\cdot}02$	$0{\cdot}34 \pm 0{\cdot}02$
$2{\cdot}0 \times 10^{-5}$	$0{\cdot}76 \pm 0{\cdot}01$	$0{\cdot}54 \pm 0{\cdot}01$
$3{\cdot}0 \times 10^{-5}$	$0{\cdot}94 \pm 0{\cdot}01$	$0{\cdot}61 \pm 0{\cdot}01$
$9{\cdot}0 \times 10^{-5}$	$0{\cdot}98 \pm 0{\cdot}01$	$0{\cdot}81 \pm 0{\cdot}01$
$1{\cdot}0 \times 10^{-3}$	$0{\cdot}97 \pm 0{\cdot}01$	1·00*

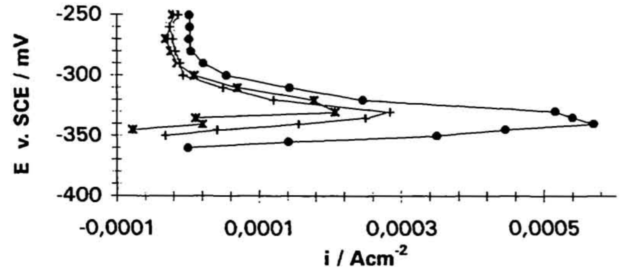
* Within the experimental precision.



a b c d

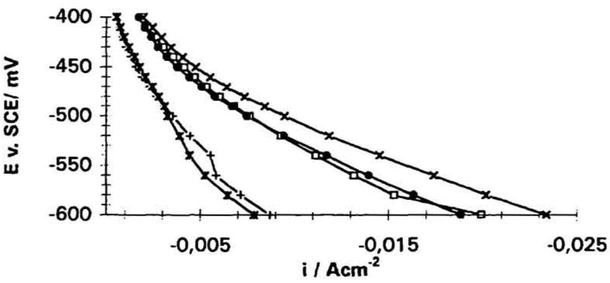
a ×100; *b* ×1000; *c* ×2000; *d* ×3300

2 *Scanning electron micrographs at given magnifications of type 304 SS after immersion in unstirred 2M H_2SO_4 solution containing $1{\cdot}0 \times 10^{-3}$M benzotriazole*



● 0; + $6{\cdot}5\times10^{-6}$M; ∗ $1{\cdot}0\times10^{-5}$M

3 *Potentiostatic anodic polarisation curves for type 304 SS in 2M H_2SO_4 solution for given concentrations of benzotriazole (below transpassive region)*



× 0; □ $6{\cdot}5\times10^{-6}$M; ∗ $1{\cdot}0\times10^{-5}$M; + $2{\cdot}0\times10^{-5}$M; ● $3{\cdot}0\times10^{-5}$M

5 *Potentiostatic cathodic polarisation curves for type 304 SS in 2M H_2SO_4 solution for given concentrations of benzotriazole*

content of ~90·0% (relative to the total content of iron, manganese, chromium, and nickel), suggesting the dissolution of iron rich inclusions.

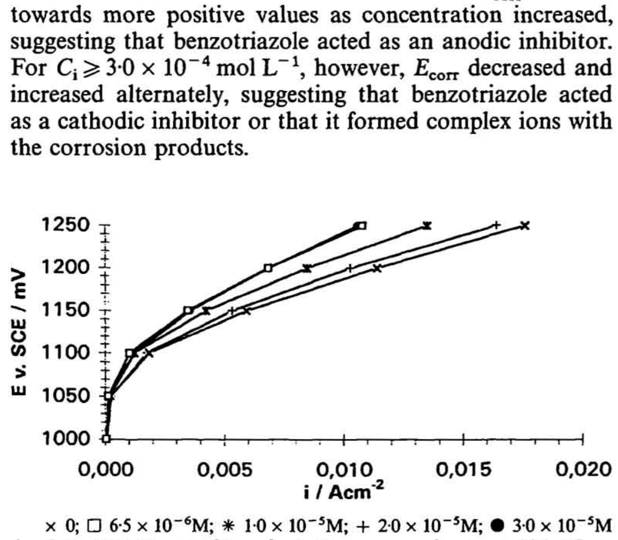
A quantitative analysis unit (Quantimet) coupled to an optical microscope detected a metallic surface area with inclusions of ~3·5%.

Figure 2 shows the 304 SS surface after immersion for 1 h in 2M H_2SO_4 solutions containing $1{\cdot}0\times10^{-3}$M benzotriazole without stirring. It can be seen, in this case, that the inclusions did not dissolve. Analysis by SEM linked to inclusion counting can explain the different θ_{max} values for stirred and unstirred solutions. When the concentration of benzotriazole is $1{\cdot}0\times10^{-3}$ mol L^{-1} and the solution has not been stirred, the low mass transport rate completely prevents dissolution of inclusions and raises the value of θ_{max} to 1·0.

Corrosion potential E_{corr} values were obtained from open circuit potential values with respect to time for type 304 SS in 2M H_2SO_4 solutions with different concentrations of benzotriazole. The values of E_{corr}, measured in millivolts with respect to the SCE, for the different concentrations, in moles/litre, were:

0	-351 ± 7
$6{\cdot}5\times10^{-6}$	-31 ± 11
$1{\cdot}0\times10^{-5}$	29 ± 4
$3{\cdot}0\times10^{-5}$	40 ± 2
$9{\cdot}0\times10^{-5}$	107 ± 10
$3{\cdot}0\times10^{-4}$	23 ± 4
$5{\cdot}0\times10^{-4}$	49 ± 12
$7{\cdot}0\times10^{-4}$	53 ± 2
$1{\cdot}0\times10^{-3}$	189 ± 27
$1{\cdot}0\times10^{-2}$	45 ± 40

For lower benzotriazole concentrations E_{corr} tended towards more positive values as concentration increased, suggesting that benzotriazole acted as an anodic inhibitor. For $C_i\geqslant3{\cdot}0\times10^{-4}$ mol L^{-1}, however, E_{corr} decreased and increased alternately, suggesting that benzotriazole acted as a cathodic inhibitor or that it formed complex ions with the corrosion products.



× 0; □ $6{\cdot}5\times10^{-6}$M; ∗ $1{\cdot}0\times10^{-5}$M; + $2{\cdot}0\times10^{-5}$M; ● $3{\cdot}0\times10^{-5}$M

4 *Potentiostatic anodic polarisation curves for type 304 SS in 2M H_2SO_4 solution for given concentrations of benzotriazole (including transpassive region)*

Figures 3–5, in which i represents current density, show anodic and cathodic potentiostatic polarisation curves for type 304 SS in 2M H_2SO_4 in unstirred solutions, in the absence and presence of different benzotriazole concentrations. Figures 3 and 4 show that benzotriazole acted as an inhibitor over the entire range of potentials more positive than E_{corr}. The current density values decreased as benzotriazole concentration increased, although the transpassivation potential value remained unaffected. Figure 5 shows the effect of benzotriazole as a cathodic inhibitor. The value of θ was 0·70 at -580 mV according to the equation

$$\theta=(i_0-i_i)/i_0$$

where i_0 and i_i represent the current density in the absence and presence of $3{\cdot}0\times10^{-5}$M benzotriazole.

The stability of the inhibitive film formed on the metallic surface was tested. Weight loss experiments were carried out in 2M H_2SO_4 solutions containing 1mM benzotriazole. After 1 h, the type 304 SS specimens were removed and immersed in 2M H_2SO_4 solutions without benzotriazole. There was no measurable weight loss after 7 days, indicating that the inhibitor film was stable and adherent.

CONCLUSIONS

1. Benzotriazole is an effective corrosion inhibitor for type 304 SS in 2M H_2SO_4 solution at a room temperature of 27 ± 2°C. It covered all the metallic surface and did not promote selective dissolution.

2. Benzotriazole acted as an inhibitor over the entire range of potentials studied from -625 to $+1250$ mV, including the transpassivation region.

3. The inhibitive film obeyed the Langmuir isotherm and the K_{ads} value of $\sim10^5$ mol^{-1} L suggests chemical adsorption.

4. The value of θ_{max} was 0·97 for stirred solutions and 1·0 for unstirred solutions, these values being associated with the partial dissolution and lack of dissolution of inclusions respectively.

5. The inhibitive film was stable and adherent and remained on the metallic surface if the specimen was subsequently immersed in 2M H_2SO_4 solutions without benzotriazole.

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