Benzotriazole as corrosion inhibitor for type 304 stainless steel in water–ethanol media containing 2M H_2SO_4

P. R. P. RODRIGUES
A. H. P. DE ANDRADE
S. M. L. AGOSTINHO

The effect of benzotriazole (BTAH) as a corrosion inhibitor for type 304 stainless steel in 2M H_2SO_4 water–ethanol (80:20) solutions has been studied using weight loss experiments, anodic and cathodic potentiostatic measurements, and analysis by scanning electron microscopy (SEM). BTAH increases the corrosion rate at lower concentrations ($\leqslant 3{\cdot}0 \times 10^{-6}$M) but it provides complete inhibition when [BTAH] $\geqslant 1{\cdot}5 \times 10^{-4}$M. The catalytic effect was also observed from anodic potentiostatic curves for [BTAH] $\leqslant 10^{-6}$M over the entire active potential range. A synergistic effect was observed in the presence of ethanol for higher BTAH concentrations when the system was compared with those in aqueous media. BTAH acts as a cathodic and anodic inhibitor over the entire range of potentials studied.

Dr Rodrigues and Dr Agostinho are at IQUSP – the Institute of Chemistry, University of São Paulo, CEP 05599-970, CP 26.077, São Paulo, Brazil, and Dr de Andrade is at IPEN/CNEN – the Institute of Energetic and Nuclear Research/Brazilian Nuclear Energy Commission, CEP 05422-970, CP 11.049, São Paulo, Brazil. *Manuscript received 10 July 1996.*

INTRODUCTION

The electrochemical behaviour of iron alloys in water–ethanol media has been studied in connection with their application in equipment for the transportation of organic solvents and in various chemical industry and laboratory applications. Such studies are clearly of great practical importance.

The literature contains references to many investigations on the corrosion resistance of stainless steels in H_2SO_4 both in aqueous and water alcohol media.[1–3] However, there have been few publications concerning the effect of corrosion inhibitors in these systems. The effect of benzotriazole (BTAH) as a corrosion inhibitor in aqueous media containing different H_2SO_4 concentrations has been shown in many recent studies of type 347 stainless steel (SS)[4] and type 304 SS.[5–7]

The present paper reports a study of the inhibitive efficiency of BTAH on type 304 stainless steel in water–ethanol solutions (80:20 volume ratio) containing 2M H_2SO_4. The techniques used included weight loss experiments, open circuit potential measurements, anodic and cathodic potentiostatic polarisation curves, and microscopic analysis.

EXPERIMENTAL

The composition of the type 304 SS used in the present study was Fe–0·075C–0·47Si 1·28Mn–17·99Cr–0·07Mo–8·00Ni–0·11Co–0·04V <0·05W (wt-%). Rectangular specimens with an area of 20 cm^2 were used for weight loss measurements, and working electrodes with an area of 2 cm^2 were employed in the electrochemical measurements.

The electrodes were successively polished with 320, 400, and 600 grade emery papers, washed with water and ethanol, and air dried for both the weight loss experiments and the potentiostatic studies. The electrochemical test cell, of 1 L volume, contained a Luggin capilliary, a saturated calomel reference electrode (SCE), and a large area platinum foil as an auxiliary electrode. The solutions were prepared from analytical grade reagents and double distilled water. The ethanol concentration present in the water–ethanol solutions (80:20) was evaluated with a 23 mL Sprengel–Ostwald picnometer.[8] The working electrode was polished and the solutions were changed before each experiment. A magnetic stirrer was employed when needed. The electrodes were immersed in the solution for a period of 1 h.

Specimens for analysis by scanning electron microscopy (SEM) were polished to a 1 μm surface finish using diamond paste. A model XL 30 Phillips SEM was used in microscopic analysis. Potentiostatic measurements were made using a model PEC 1 potentiostat manufactured by the Aardvark Inst. Co. Inc. All experiments were carried out at room temperature (27 ± 2°C).

RESULTS AND DISCUSSION

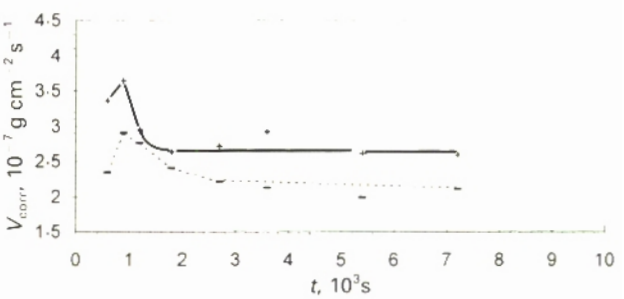
Figure 1 presents corrosion rates calculated from equation (1) for type 304 SS in aqueous and water–methanol solutions of 2M H_2SO_4 for various immersion times

$$V_{corr} = \{(1/A)\,\Delta m/\Delta t\} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where A is the electrode area, Δm is the metal weight loss, and Δt is the metal immersion time in the solution.

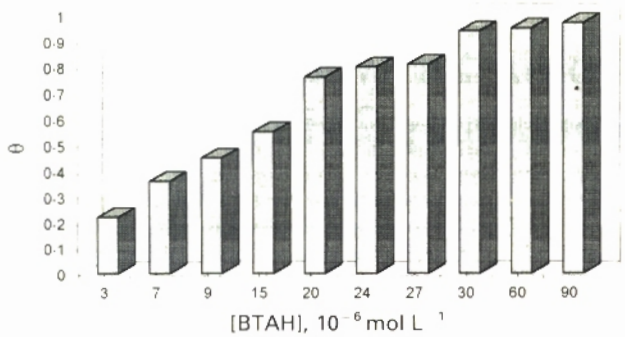
Steady state corrosion rates are achieved after different exposure times following a change of solvent and these are more rapidly attained in the aqueous solution. It can also be seen from Fig. 1 that V_{corr} is higher in the aqueous medium than in the water ethanol medium.

Weight loss experiments were conducted without stirring the solution. Nine specimens of type 304 SS were first exposed in water–ethanol solutions containing 2M H_2SO_4 + $1{\cdot}5 \times 10^{-4}$M BTAH for a 1 h immersion time. After the exposure, all nine specimens were removed from the solution. Five of the specimens were then immersed in 2M H_2SO_4 water–ethanol (80:20) solutions without BTAH and the other four were immersed in aqueous 2M H_2SO_4



+ 2M H_2SO_4 aqueous solutions; – 2M H_2SO_4 water–ethanol (80:20) solutions

1 *Corrosion rates at different immersion times for type 304 SS in stirred solutions*



2 *Inhibitive efficiency as function of BTAH concentration in stirred 2M H_2SO_4 aqueous media*

solutions without BTAH. After 24 h, all of the specimens were shown to be protected and the weight losses were not measurable. These results prove that BTAH protects the material and that the inhibitive film is stable and resistant even during subsequent exposure in the absence of BTAH from the solution.

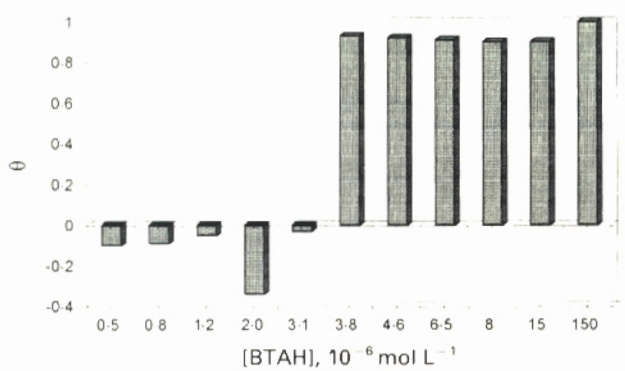
Figures 2 and 3 show values of inhibitor efficiency θ calculated from equation (2) for aqueous and water–ethanol solutions respectively

$$\theta = \{(V_0 - V_i)/V_0\} \quad \ldots\ldots\ldots\ldots \quad (2)$$

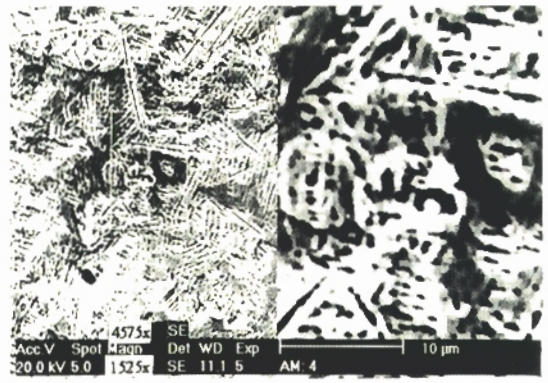
where V_0 and V_i represent the corrosion rate in the absence and in the presence of BTAH respectively.

It is worth noting the different behaviour of the interface when only the solvent composition is changed. In aqueous media the inhibitive effect increases as the concentration of inhibitor, BTAH, increases. In water–ethanol media for $[BTAH] \leqslant 3{\cdot}1 \times 10^{-6}$M a catalytic effect is observed with a maximum at $[BTAH] = 2{\cdot}0 \times 10^{-6}$M. It is important to note that the maximum catalytic effect is observed when V_i in the water ethanol medium is equal to V_0 in the aqueous medium. The inhibitive effect is significant for $[BTAH] \geqslant 3{\cdot}8 \times 10^{-6}$M. A 100% inhibitor efficiency was observed for $[BTAH] = 0{\cdot}15$ mM in the water–ethanol medium.

The SEM technique was used to verify the occurrence or otherwise of inclusion dissolution both in the presence and absence of BTAH. Figures 4 and 5*a* and *b* show the partial dissolution and absence of dissolution of inclusions present on the 304 SS surface in the absence and in the presence of BTAH respectively. These results are different from those observed in aqueous media, where the maximum inhibitor efficiency is 97% and partial dissolution of inclusions occurs in the presence of BTAH.[7] A synergistic effect of ethanol and BTAH could be responsible for the absence of dissolution of inclusions and for the higher inhibitor efficiency for $[BTAH] \geqslant 3{\cdot}8 \times 10^{-6}$M in water–ethanol media.



3 *Inhibitive efficiency as function of BTAH concentration in stirred 2M H_2SO_4 water–ethanol (80 : 20) solutions*



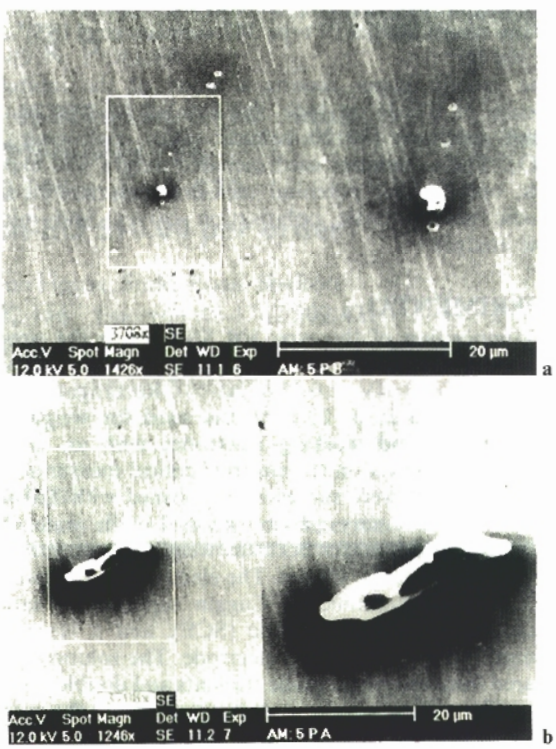
4 *Micrograph (SEM) of type 304 SS after 1 h immersion in stirred 2M H_2SO_4 water–ethanol (80 : 20) solutions in absence of BTAH*

The corrosion potential E_{corr} values for 304 SS in 2M H_2SO_4 water–ethanol (80 : 20) solutions in the absence and presence of BTAH are as follows:

BTAH, M	E_{corr}, mV(SCE)
0	-371 ± 001
$7{\cdot}7 \times 10^{-7}$	-349 ± 004
$2{\cdot}0 \times 10^{-6}$	-364 ± 001
$8{\cdot}0 \times 10^{-6}$	$+034 \pm 010$
$1{\cdot}5 \times 10^{-4}$	-052 ± 009

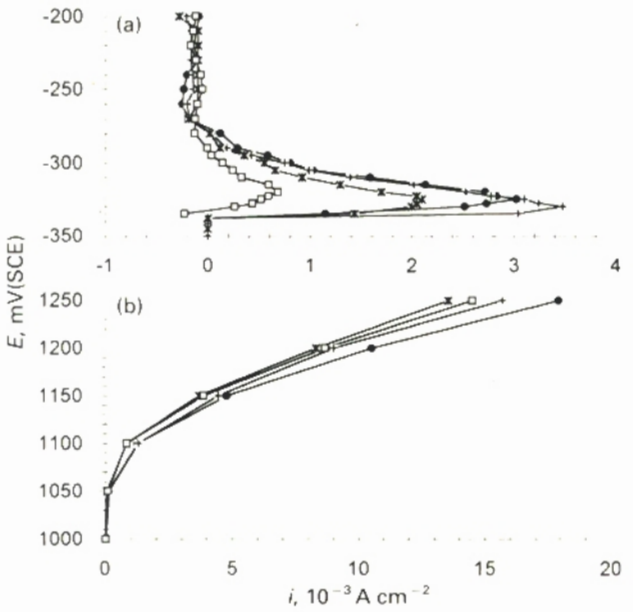
It can be seen that for $[BTAH] \geqslant 8{\cdot}0 \times 10^{-6}$M there is about +300 mV change in the E_{corr} values, suggesting that it acts as an anodic inhibitor.

Figures 6*a* and *b* and 7 show anodic and cathodic potentiostatic polarisation curves for type 304 SS in 2M H_2SO_4 water–ethanol solutions in the absence and presence of different BTAH concentrations. It can be seen from Fig. 6*a* that critical current density values i_c increase for $[BTAH] \leqslant 2{\cdot}0 \times 10^{-6}$M. These results show the catalytic effect at lower BTAH concentrations, in accordance with



a equiaxed inclusion; *b* elongated inclusion

5 *Micrograph (SEM) of type 304 SS after 1 h immersion in stirred 2M H_2SO_4 water–ethanol (80 : 20) solutions in presence of $1{\cdot}5 \times 10^{-4}$M BTAH*



● 0 M; + $2{\cdot}0 \times 10^{-6}$ M; * $4{\cdot}0 \times 10^{-6}$ M; □ $1{\cdot}0 \times 10^{-5}$ M
a transpassive region not included; *b* passive–transpassive region

6 *Anodic potentiostatic polarisation curves of type 304 SS in unstirred 2M H_2SO_4 water–ethanol solutions (80 : 20) in presence of BTAH*

those obtained from weight loss experiments. However, for $[BTAH] > 2{\cdot}0 \times 10^{-6}$ M, i_c decreases as [BTAH] increases, indicating its inhibitive effect. BTAH is also an anodic inhibitor in the transpassive region. Figure 7 shows that BTAH acts as a cathodic inhibitor over the entire range of BTAH concentrations studied.

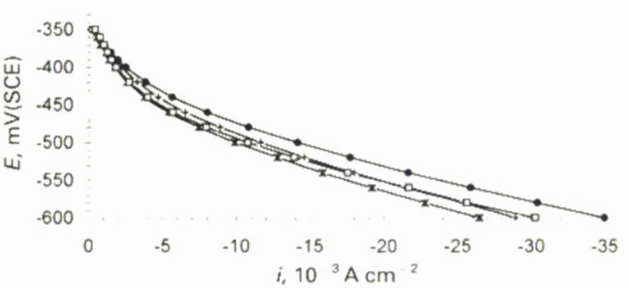
CONCLUSIONS

The results of this work allow the following conclusions to be drawn.

1. Type 304 SS in 2M H_2SO_4 water–ethanol solutions undergoes general corrosion.

2. The effect of BTAH on the interface depends on its concentration: for $[BTAH] \leqslant 3{\cdot}1 \times 10^{-6}$ M it causes a catalytic effect and above this concentration it acts as an inhibitor.

3. The higher efficiencies at relatively low BTAH concentrations in water–ethanol media as compared with aqueous media suggest a synergistic effect of ethanol on the inhibitive action of BTAH.



● 0 M; + $2{\cdot}0 \times 10^{-6}$ M; * $4{\cdot}0 \times 10^{-6}$ M; □ $1{\cdot}0 \times 10^{-5}$ M

7 *Potentiostatic cathodic polarisation curves of type 304 SS in unstirred 2M H_2SO_4 water–ethanol solutions (80 : 20) in presence of BTAH*

4. The maximum inhibition efficiency, 100%, was observed in water–ethanol media for [BTAH] = 0·15 mM.

5. BTAH acts as both an anodic and cathodic inhibitor for type 304 SS in a 2M H_2SO_4 water–ethanol (80 : 20) medium.

6. The previously formed film in a 2M H_2SO_4 water–ethanol solution containing $1{\cdot}5 \times 10^{-4}$ M BTAH is stable and continues to protect the metallic surface in the same corrosive solution, with or without ethanol, even in the absence of BTAH.

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