1,2,4,5 tetrazo spiro (5,4) decane-3 thione as a corrosion inhibitor for arsenical aluminium brass in 3.5% NaCl solution

L. John Berchmans
S. Venkatakrishna Iyer
V. Sivan and
M.A. Quraishi

The authors

L. John Berchmans and S. Venkatakrishna Iyer are both based at the Central Electrochemical Research Institute, Karaikudi, India.
V. Sivan is based in the Department of Metallurgical Engineering, Regional Engineering College, Tiruchirappalli, India.
M.A. Quraishi is based in the Department of Applied Chemistry Z.H. College of Engineering and Technology, Aligarh Muslim University, Aligarh (UP), India.

Keywords

Corrosion inhibitors, Copper, Alloys

Abstract

The influence of a newly synthesised organic compound on the inhibition of corrosion of arsenical aluminium brass in a NaCl solution has been investigated using weight loss measurements, potentiodynamic polarization studies and impedance measurements. Different corrosion kinetic parameters obtained from polarisation studies reveal that the inhibition of corrosion of arsenical aluminium brass in NaCl is under mixed control. UV-reflectance, X-ray diffraction and scanning electron microscopic studies have also been carried out to understand the mechanism of inhibition of corrosion, and also the morphological changes on the surface of the alloy. The adsorption of this compound on the metal surface from 3.5% NaCl solution is found to obey Temkin's adsorption isotherm.

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Introduction

Copper and its alloys, especially brasses have been used as materials for the construction of tubes and pipes for transporting water and also for fabricating condensers and heat exchangers (Unni *et al.*, 1982; Deshmukh *et al.*, 1982; Vakil and Oza, 1982). Aluminium brass is finding extensive use as the tube material for condensers and heat exchangers making use of sea or brackish water as the coolant (Habib and Amin, 1992; Narain and Asad, 1992; Shalaby *et al.*, 1996; Epler and Castle, 1979; Castle and Parvizi, 1986). Incorporation of arsenic and/or phosphorus as the minor alloying additive is found to bring down the occurrence of dealloying attack (Pryor and Glam, 1982; Mazza and Torchio, 1983). The greater resistance of aluminium brass may be attributed to the presence of an aluminium compound which has a passivating effect (Baccaria and Poggi, 1988; Baccaria *et al.*, 1989). Usually brass is susceptible to a corrosion process namely dezincification. Many organic compounds have been examined for their utility as corrosion inhibitors for brasses in different corrosive media. Azoles have been found to serve as effective inhibitors for the corrosion of brasses in acidic and neutral solutions (Patel *et al.*, 1974; Soni and Bhatt, 1974; Elrahman, 1991; Dacosta *et al.*, 1993; Heidersback and Vernick, 1972; Farooqi and Quaraishi, 1997; Berchmans *et al.*, 1997). In the present study, a new compound namely 1,2,4,5 tetrazo spiro (5,4) decane-3-thione (TSDT) has been synthesised, and its influence on the corrosion of arsenical aluminium brass in 3.5% NaCl has been studied using different techniques such as weight loss measurements, potentiodynamic polarization studies and impedance measurements. UV reflectance measurements, X-ray diffraction studies and scanning electron microscopic studies have also been carried out. Results are reported and discussed.

Experimental

Arsenical aluminium brass specimens of the composition Cu – 77.5 per cent, Zn – 20.5 per cent, Al – 1.9 per cent and As – 0.1 per cent were used for all studies. Rectangular specimens of size 5 × 2 × 0.25 cm were used

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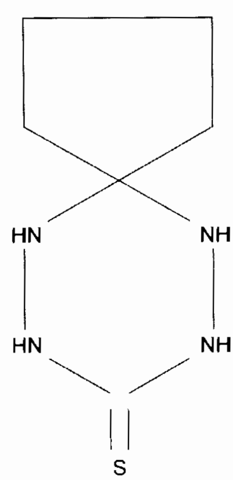
for weight loss measurements. A cylindrical rod of the same composition and embedded in Teflon to expose an area of 0.276cm^2 was used for potentiodynamic polarization studies. Specimens used for weight loss measurements were polished using mechanical polishing and then degreased. For polarization studies the electrode was polished using a sequence of emery papers and then degreased. The compound used as inhibitor, namely, 1,2,4,5 tetrazo spiro (5,4) decane-3-thione (TSDT) was synthesised according to the procedure reported elsewhere (Lemon, 1969). The structural formula of the compound is given in Figure 1. The compound has the molecular formula $C_6N_4H_{12}S$, and a molecular wt of 172.00. A.R. grade B.D.H. NaCl was used for preparing all solutions. Double distilled water was used for preparing experimental solutions.

Both weight loss and potentiodynamic polarization studies were carried out as described elsewhere (Phani *et al.*, 1995). Impedance measurements were carried out *using a Frequency analyser (Model 170* Solartron, UK) at the corrosion potential and the Electrochemical interface (Model 1186, Solartron, UK) as described elsewhere (Phani *et al.*, 1995). Surfaces of corroded and inhibited specimens were examined by UV reflectance measurements using U-3400 Spectrometer (UV-VIS-NIR Spectrometer, Hitachi, Japan) as reported earlier (Berchmans *et al.*, 1997). Corrosion products adhering to the surface were examined by X-ray diffractometry (Model JEOL 8030) using copper K_α (A = 1.541Å) as the target material.

Figure 1 Structural formula 1,2,4,5-tetrazo spiro decane-3-thione



Results and discussion

Table I gives the values of inhibition efficiency for different concentrations of TSDT for the corrosion of arsenical aluminium brass in 3.5 per cent NaCl. It is found that the inhibition efficiency increases with increase in the concentration up to 500ppm. Beyond this concentration, there is no appreciable increase in the inhibition efficiency. The inhibition of corrosion of arsenical aluminium brass in 3.5 per cent NaCl solution can be attributed to the adsorption of the compound on the metal surface. The adsorption can occur through the interaction between the lone pairs of electrons of sulphur and nitrogen atoms and the positively charged metal surface.

The degree of surface coverage (θ) for different concentrations of TSDT has been evaluated using the equation θ = 1-Winh/W from weight loss values in the absence (W) *and presence of TSDT (Winh). The data* obtained were tested graphically for fitting a suitable adsorption isotherm. Temkin's isotherm was tested by plotting θ vs log C. A straight line was obtained, thereby proving that the adsorption of TSDT on arsenical aluminium brass from NaCl solution obeys Temkin's adsorption isotherm.

Table II gives the values of inhibition efficiency, in the presence of different concentrations of TSDT for different temperatures ranging from 30°C to 90°C. It is found that the inhibition efficiency decreases with an increase in the temperature. This observation can be attributed to the desorption of the TSDT from the metal surface at higher temperatures. Therefore,

Table I Inhibition efficiencies for the corrosion of arsenical aluminium brass in 3.5% NaCl in the presence of different concentrations of 1,2,4,5 tetrazo spiro (5,4) decane-3-thione (TSDT)

Concentration of the inhibitor (in ppm)	Inhibition efficiency (%)
50	46.3
100	59.0
200	73.0
300	84.0
400	92.3
500	93.3
600	93.5
700	93.7

Note: Temp. 30 ± 2°C

Table II Values of inhibition efficiency (%) for different concentrations of 1,2,4,5 tetrazo spiro (5,4) decane-3-thione (TSDT) at different temperatures

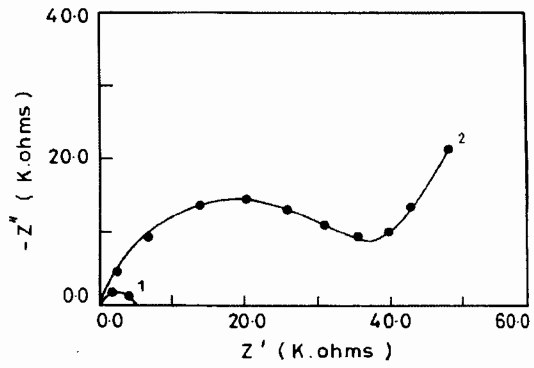
Concentration of the inhibitor (ppm)	Values of inhibition efficiency (%) at different temperatures 30°C	50°C	70°C	90°C
50	46.3	45	43.6	42.8
100	59.0	54.6	49.0	42.7
200	73.1	68.2	67.3	65.5
300	84.0	82.0	78.7	69.5
400	92.3	87.0	84.4	79.2
500	93.3	88.0	83.0	79.0

this compound is not very effective as a corrosion inhibitor at higher temperatures.

Table III gives the values of corrosion kinetic parameters such as corrosion current density (I_{corr}), corrosion potential (E_{corr}), Tafel slopes (b_a and b_c) and inhibition efficiency calculated from the corrosion current densities derived from potentiodynamic polarization studies. Values of E_{corr} shift to less negative values in the presence of increasing concentrations of TSDT. An increase in the concentration of TSDT is found to increase the values of both Tafel slopes almost to an equal extent. So the inhibition of corrosion of arsenical aluminium brass in 3.5 per cent NaCl solution is under mixed control. Values of inhibition efficiency obtained from the weight loss method and the values of I_{corr} agree very well.

The Nyquist plot (Figure 2) in the presence of 500ppm TSDT shows Warburg impedance, thereby bringing out the fact that the reaction is under diffusion control involving ionic diffusion. This situation usually occurs when the metal surface is covered with a reaction product of limited solubility.

Figure 2 Nyquist plot for aresnical aluminium brass in 3.5 per cent NaCl in the presence of 500ppm TSDT



Note: 1 = 3.5% NaCl alone; 2 = 3.5% NaCl + 500 ppm TSDT

The fact that the inhibition of corrosion of arsenical aluminium brass in 3.5 per cent NaCl in the presence of TSDT may be due to the formation of an almost insoluble film on the metal surface is supported by UV reflectance studies carried out using different specimens under similar conditions. A comparison of reflectance curves for buffed and well polished arsenical aluminium brass specimens with those dipped in 3.5 per cent NaCl in the absence and presence of TSDT (Figure 3) clearly brings out the fact that the percentage of reflectance is maximum for the polished specimen. It has been considerably decreased for the specimen immersed in 3.5 per cent NaCl solution. This change can be attributed to the change in surface characteristics due to the corrosion of specimen in NaCl. But in the presence of 500ppm TSDT, the reflectance is decreased only to a very small extent. This shows that

Table III Corrosion kinetic parameters for the inhibition of arsenical aluminium brass in 3.5% NaCl in the presence of different concentrations of 1,2,4,5 tetrazo spiro (5,4) decane-3-thione (TSDT) at 30 ± 1°C

Inhibitor concentration (in ppm)	E_{corr} (mV)	I_{corr} (mA.cm^{-2})	Tafel slope b_a (mV. dec^{-1})	b_c	Inhibition efficiency (%)
Blank	−257	3.9	34.8	52.4	–
50	−250	2.0	35.2	53.6	48.7
100	−245	1.75	35.8	54.2	55.2
200	−245	1.05	37.2	55.8	73.1
300	−242	0.65	40.4	59.2	85.9
400	−238	0.48	43.5	61.6	87.6
500	−235	0.35	45.2	63.7	91.0
600	−230	0.24	46.3	64.9	93.8
700	−230	0.19	47.2	65.2	95.1

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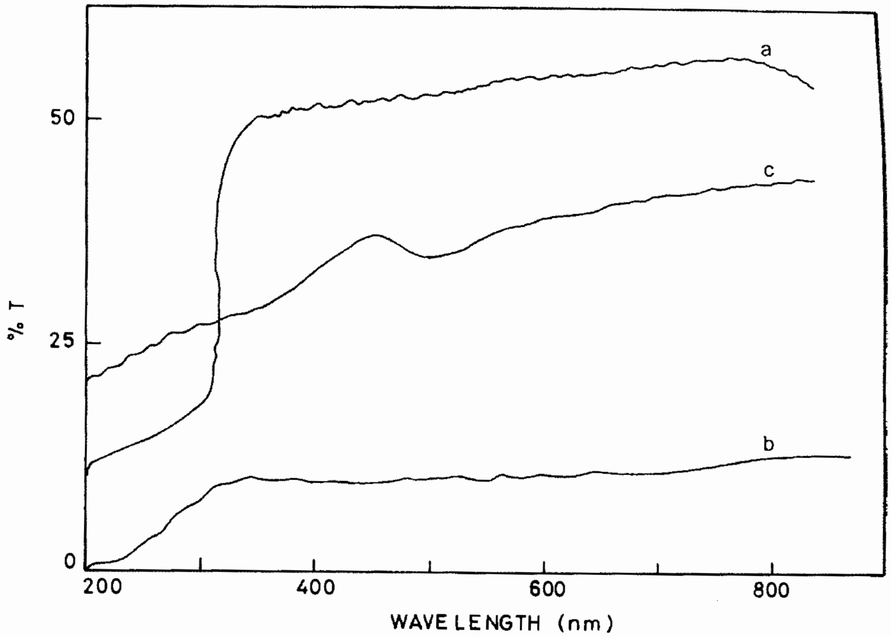
Figure 3 Reflectance curves for arsenical aluminium brass specimens under various conditions



Note: a = polished; b = immersed in 3.5% NaCl solution; c = immersed in 3.5% NaCl solution containing TSDT (500 ppm)

the surface characteristics of the inhibited of arsenical aluminium brass specimen are not altered very much because of the formation of a film by the adsorption of TSDT on the metal surface.

X-ray diffraction studies (Figure 4(a)) on the corroded specimen clearly show the formation of an outer oxide layer consisting of cuprous oxide and copper oxychloride (2θ = 45,50). XRD spectrum (Figure 4(b)) for arsenical aluminium brass in 3.5 per cent NaCl solution in the presence of TSDT shows the presence of an adsorbed film which is responsible for the inhibition of corrosion of the metal. This inference can be drawn from the fact that there is a difference in the peak heights in the spectra obtained in the presence and absence of TSDT.

SEM photographs also show the formation of a thin organic film on the metal surface, which is actually responsible for the inhibition of corrosion of the metal in NaCl solution.

Figure 4(a) XRD spectrum for arsenical aluminium brass dipped in 3.5% NaCl solution

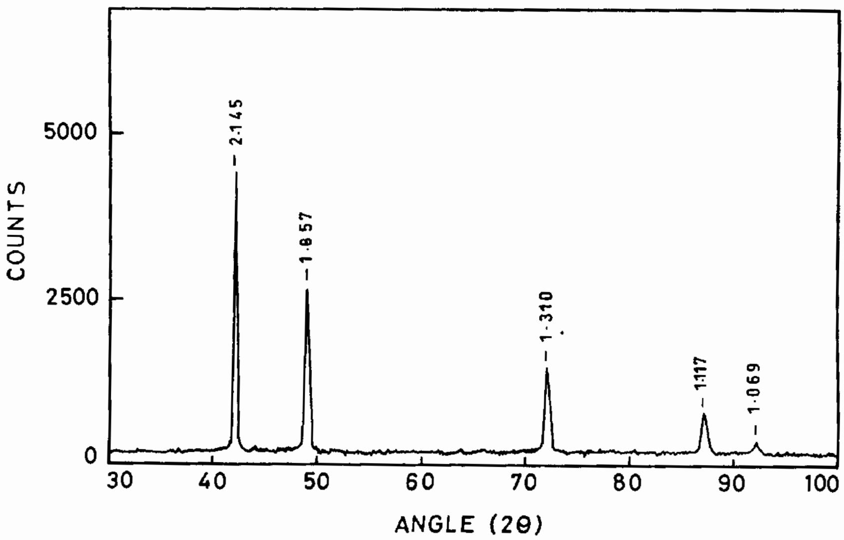
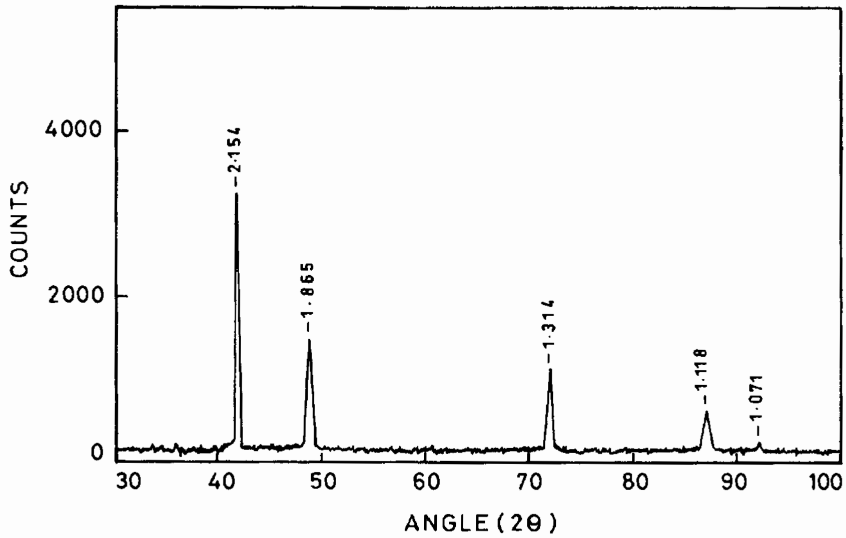


Figure 4(b) XRD spectrum for arsenical aluminium brass in 3.5% NaCl with the presence of 500ppm TSDT



Conclusion

Studies on the inhibition of corrosion of arsenical aluminium brass in 3.5 per cent NaCl by TSDT bring out the following main conclusions:

(1) 1,2,4,5 tetrazo spiro (5,4) decane-3-thione (TSDT) very effectively inhibits the corrosion of arsenical aluminium brass in 3.5% NaCl.
(2) The inhibition of corrosion of arsenical aluminium brass in NaCl by TSDT is under mixed control.
(3) The adsorption of TSDT on the surface of aluminium brass from NaCl solution obeys Temkin's adsorption isotherm.
(4) Impedance measurements and UV reflectance studies bring out the fact that the inhibition is due to the formation of a thin insoluble film on the metal surface.
(5) An increase in temperature brings down the inhibitive performance of the compound.

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