Inhibition of corrosion of copper by 5-mercapto-3-p-nitrophenyl-1,2,4-triazole in aqueous environment

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Keywords

Copper, Corrosion, Corrosion inhibitors

Abstract

The inhibitor 5-mercapto-3-p-nitrophenyl-1-2-4-triazole has 92.75 per cent inhibition efficiency in controlling corrosion of copper in neutral aqueous environment, containing 300 ppm Cl^-, a situation where the chloride concentration of the cooling water system will usually be not greater than 300 ppm. A discussion of mechanistic aspects of corrosion inhibition is based, in a holistic way, on the results obtained from the classical weight loss method, potentiostatic polarisation study, AC-impedance study, UV-visible absorption study and different surface examination techniques like FTIR, XRD and ESCA. The protective film is found to be of unimolecular thickness and to consist of Cu (I) – inhibitor complex cuprous chloride, CuCl or $CuCl_2^-$ complex ion or both and no oxide of copper on the surface.

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It is clear from the literature survey that organic compounds containing hetero atoms like oxygen, nitrogen and sulphur are very good corrosion inhibitors (Nandeesh and Seshadri, 1988) for several metals including copper. Benzotriazole (BTA) (Fiaud and Ghimouj, 1989), tolytriazole (TTA) (Walker, 1975), benzimidazole (Lewis, 1982), thiazoles (Hashmi and Hogarth, 1988) and their derivatives (Trabanelli and Carasitti, 1970; Ravi *et al.*, 1986) are some examples of very good inhibitors. 1,2,4-benzotriazole (BTA) and mercaptobenzothiazole (MBT) are the most widely used corrosion inhibitors for copper in cooling water systems (ASM Handbook, 1992). In the present work, the inhibitive effect of 5-mercapto-3-p-nitrophenyl-1,2,4-triazole in controlling the corrosion of copper in aqueous environment at various chloride concentrations in the range 50-300 ppm and at various pH values in the range 6.0 to 9.0 has been studied using the weight loss method. A suitable mechanism of corrosion inhibition has been proposed based on the results obtained from potentiostatic polarisation study, AC-impedance study, UV-Visible absorption study, FTIR, XRD and ESCA spectra.

Experimental

Preparation of specimens

Pure copper specimens (99.99 per cent purity) from the same copper sheet of dimensions 4.0 × 1.0 × 0.2cm were polished to mirror finish, degreased with acetone and used for weight loss and surface examination studies. For potentiostatic polarisation studies a copper rod encapsulated in Teflon with an exposed cross section of 0.5cm diameter was used as the working electrode. Its surface was polished to mirror finish and degreased with trichloroethylene.

Weight loss method

Copper specimens, in triplicate, were immersed in 100ml test solutions containing various concentrations of the inhibitor both in the absence and presence of the inhibitor for a period of ten days. The weights of the

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specimens before and after immersion were determined using a Mettler Analytical Balance (E.Mettler, Zurich), with a readability of 0.01mg.

Potentiostatic polarisation study

This study was carried out in a three-electrode cell assembly connected to bioanalytical system (BAS-100A), electrochemical analyser, provided with iR compensation facility, using copper as working electrode, platinum as the counter electrode and saturated calomel electrode as the reference electrode.

AC-impedance study

AC-impedance studies were carried out in a three electrode cell assembly using computer controlled EG&G Princeton Applied Research Model 6310, using copper as the working electrode, platinum as counter electrode and saturated calomel electrode as the reference electrode.

UV-visible spectra

The UV-visible absorption spectra of various solutions before and after immersion of the metal specimen for ten days were recorded using the Shimadzu model UV-160 A spectrophotometer.

Surface examination study

The copper specimens were immersed in various test solutions for a period of ten days. After ten days, the specimens were taken out, washed with water and dried. The nature of the film formed on the surface of the metal specimens was analysed by various surface analysis techniques.

FTIR spectrum

The FTIR spectrum of the film formed on the surface of metal specimen was recorded using Shimadzu 8201 PC FTIR spectrophotometer.

XRD

The XRD pattern of the surface film formed on copper specimen was recorded by using a computer controlled X-ray powder diffractometer. JEOL JDX 8030, with Cu K_α (Ni-filtered) radiation ($\lambda = 1.5418A^\circ$) at a rating of 40kV, 20mA.

ESCA

The ESCA patterns of protective films formed on the surface of copper plates were recorded using ESCA-LAB Mk-II, VG Scientific Limited, UK with Mg K_α radiation at a rating of 10kV, 10mA with a sensitivity of 0.2eV and a detection limit of up to 2 per cent.

Results and discussion

Analysis of the results of the weight loss method

Corrosion rates of copper in an aqueous environment at different concentrations of chloride in the range of 50-300 ppm and at various pH values in the range of 6-9 and in the absence and presence of inhibitor at various inhibitor concentrations were determined by weight loss method. The percentage inhibition efficiencies at different chloride concentrations at neutral pH are as shown in Table I.

It is found that a maximum inhibition efficiency in the range 92 to 94 per cent is obtained at 15 ppm of the inhibitor concentration at various concentrations of chloride ranging from 50 to 300 ppm at neutral pH. After reaching a maximum, it is observed that there is a decrease in inhibition efficiency with further increase in the concentration of the inhibitor. The percentage inhibition efficiencies at different chloride concentrations are shown as a function of the inhibitor concentration at neutral pH in Figure 1. The same trend is observed at other pH values in the range 6-9.

It is also observed from these studies that corrosion inhibition efficiencies usually increase with increase in pH from 7-9 and decrease with decreasing pH from 7 to 6. Nevertheless, the inhibition efficiency of the system ranges between 81.89 and 96.99 per cent in the pH range 6.5 to 9. It shows that this inhibitor is very much effective in the pH range of 6.5 to 9 and less effective at pH of 6 with an efficiency of 60.01 per cent only.

Dosage of inhibitor for maintenance of the protective film

Corrosion rates of copper with the surface consisting of the protective film, in neutral aqueous environment containing 300 ppm chloride both in the absence and presence of inhibitor and at

Table I Corrosion rates of copper in aqueous medium (pH = 7.0) at various concentrations of chloride in the absence and presence of inhibitor (results obtained by weight loss method). Inhibitor system: 5-mercapto-3-p-nitro phenyl-1,2,4-triazole

Sample no.	Cl^- conc. ppm	Inhibitor conc., ppm	Corrosion rate, mdd	Inhibition efficiency, per cent
1	50	0	0.2851	-
2	50	2	0.1137	60.12
3	50	5	0.0827	71.00
4	50	10	0.0431	84.87
5	50	15	0.0146	94.88
6	50	20	0.0204	92.85
7	50	25	0.0324	88.64
8	50	30	0.0463	83.76
1	100	0	0.2437	-
2	100	2	0.0979	59.84
3	100	5	0.0782	67.90
4	100	10	0.0437	82.06
5	100	15	0.0190	92.19
6	100	20	0.0340	86.04
7	100	25	0.0514	78.91
8	100	30	0.0731	70.01
1	150	0	0.2615	-
2	150	2	0.1075	58.88
3	150	5	0.0805	69.23
4	150	10	0.0486	81.42
5	150	15	0.0166	93.66
6	150	20	0.0292	88.82
7	150	25	0.0458	82.47
8	150	30	0.0648	75.23
1	200	0	0.3486	-
2	200	2	0.1272	63.51
3	200	5	0.0981	71.86
4	200	10	0.0584	83.24
5	200	15	0.0224	93.58
6	200	20	0.0273	92.18
7	200	25	0.0422	87.90
8	200	30	0.0690	80.21
1	300	0	0.5412	-
2	300	2	0.2032	62.46
3	300	5	0.1546	71.44
4	300	10	0.0939	82.65
5	300	15	0.0392	92.75
6	300	20	0.0663	87.75
7	300	25	0.0983	81.83
8	300	30	0.1384	74.43

various inhibitor concentrations obtained by weight loss method are given in Table II.

Corrosion inhibition efficiencies of the inhibitor, 5-mercapto-3-p-nitrophenyl-1,2,4-triazole are also given in the table.

It is evident from the data that at 2 ppm of the inhibitor concentration itself an inhibition efficiency of 92.42 per cent is achieved. A maximum inhibition efficiency of 93.66 per cent is obtained at 8 ppm of inhibitor concentration. Therefore, it can be concluded that for the maintenance of the protective film already formed on the copper surface the concentration of the inhibitor, as low as 2 ppm is sufficient.

Figure 1 Inhibition efficiency vs. concentration of inhibitor, 5-mercapto-3-p-nitrophenyl-1,2,4-triazole at pH = 7.0 and in different choloride environments

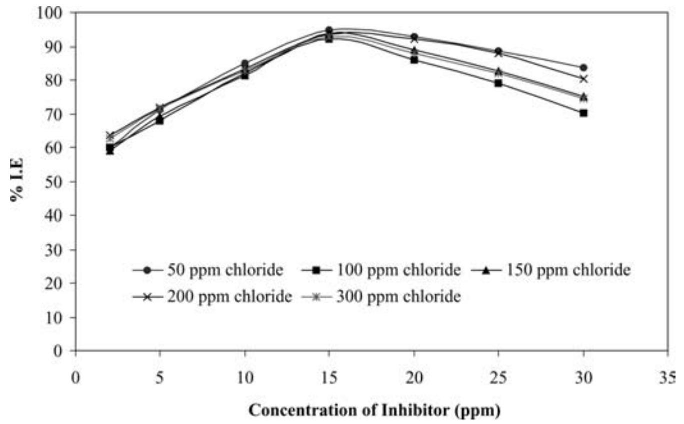


Table II Corrosion Inhibition efficiencies at various inhibitor concentrations for the maintenance of the protective film already formed on the copper surface (results obtained by weight loss method)

Sample no.	Inhibitor conc. ppm	Corrosion rate mdd	Inhibition efficiency, per cent
1	0	0.5412	-
2	2	0.0410	92.42
3	4	0.0392	92.75
4	6	0.0347	93.58
5	8	0.0343	93.66
6	10	0.0379	92.99

Notes: Environment: neutral aqueous medium containing 300 ppm chloride. Inhibitor system: 5-mercapto-3-p-nitrophenyl-1,2,4-triazole

Analysis of the results of potentiostatic polarisation study

The potentiostatic polarisation curves of copper immersed in aqueous environment in 300 ppm chloride and at various pH values in the absence and presence of the inhibitor, 5-mercapto-3-p-nitrophenyl-1,2,4-triazole are shown in Figure 2.

It is evident from the results that at pH = 6.5 there is a slight shift in corrosion potential, E_{corr} (from 88mv to 82.5mv vs. SCE) towards cathodic site. It is observed from the data that the shifts in the anodic and cathodic slopes are nearly equal indicating that this system acts as a mixed inhibitor at this pH.

At neutral pH, the corrosion potential is shifted towards anodic side (from 72.4mv to 85mv vs. SCE). When the shifts in Tafel (Tafel and Fur, 1905) slopes are compared, it can be concluded that though this system acts as a mixed inhibitor, it is predominantly cathodic in nature.

At pH = 9, the corrosion potential is shifted towards cathodic side (from 94.5mv to 63.90mv vs. SCE). It is also observed that the shift in the anodic slope is higher (19mv/decade) than the shift in cathodic slope (3mv/decade). Hence, it can be said that the same inhibitor predominantly controls the anodic reaction at pH = 9.

Analysis of the results of AC-impedance studies

The admittance plots of copper immersed in aqueous environment containing 300 ppm chloride at various values of pH (6.5, 7, and 9) in the absence and presence of the inhibitor after one hour and 24 hour immersion periods are shown in Figures 3 and 4 respectively.

Since the admittance plots are not semicircles the R_s and R_t values were calculated from the high and low frequency points of the Bode plots (log | z | vs. log f). The corresponding impedance parameters are given in Table III.

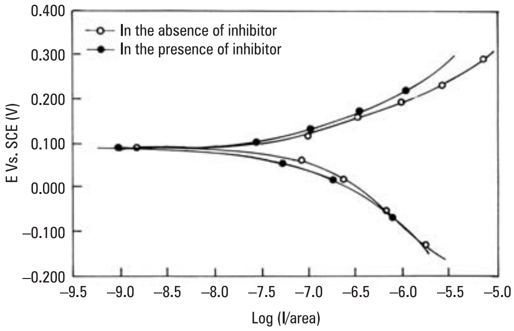
From the data, it is observed that a maximum charge transfer resistance of 171.063k ohms is obtained at pH = 9 after immersion of the sample for one hour. A maximum inhibition efficiency of 92.25 per cent is obtained at this pH. After 24 hours immersion of the sample a maximum charge transfer resistance of 371.063k ohms is achieved at pH = 9 with a maximum efficiency of 92.24 per cent. The values of corrosion inhibition efficiencies are in good agreement with the results obtained by weight loss studies. It is also noticed that there is a gradual increase in inhibition efficiency from pH = 6.5 to pH = 9 after one hour and 24 hour immersion periods.

Analysis of the UV-visible absorption spectra of solutions

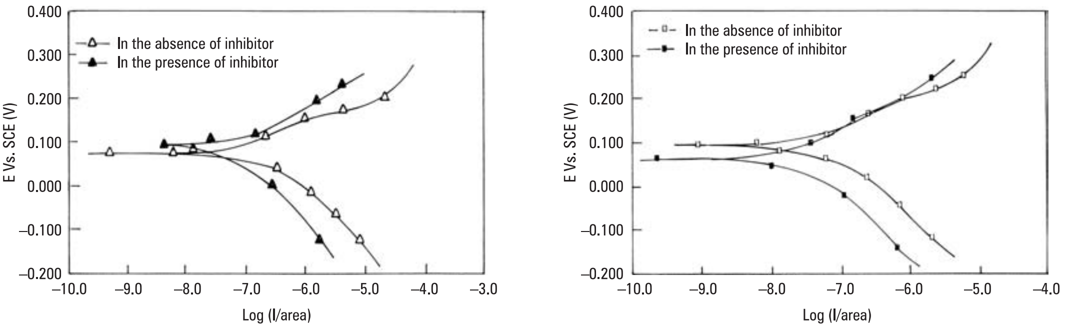
The UV-visible absorption spectra of the solutions for the inhibitor system, 5-mercapto-3-p-nitrophenyl-1,2,4-triazole in aqueous environment containing 300 ppm chloride at neutral pH before and after immersion of the copper specimens are as shown in Figure 5.

From the spectra it is clear that there is a shift in λ_{max} from curve (a) to curve (b) (301nm to 284nm) which indicates the formation of a soluble complex between the copper and the inhibitor in solution. That

Figure 2 Potentiostatic polarization curves of copper immersed in aqueous environments containing 300 ppm chloride



(a) Potentiostatic polarization curves of copper immersed in aqueous environment containing 300 ppm chloride and at pH = 6.5 in the absence and presence of the inhibitor (20 ppm) 5-mercapto-3-p-nitrophenyl – 1,2,4-triazole



(b) Potentiostatic polarization curves of copper immersed in an aqueous environment containing 300 ppm chloride and at pH = 7.0 in the absence and presence of the inhibitor (20 ppm) 5-mercapto-3-p-nitrophenyl – 1,2,4-triazole

(c) Potentiostatic polarization curves of copper immersed in an aqueous environment containing 300 ppm chloride and at pH = 9.0 in the absence and presence of the inhibitor (20 ppm) 5-mercapto-3-p-nitrophenyl – 1,2,4-triazole

means that even before the formation of a protective film, copper ions are available in solution due to initial corrosion of copper leading to the formation of a complex that could be detected by UV-visible spectroscopy.

Analysis of x-ray diffraction patterns

The XRD patterns of the films formed on the surface of copper immersed in 300 ppm chloride at neutral pH in the absence and presence of inhibitor are as shown in Figures 6 and 7 respectively.

The corresponding data for pure copper surface and for melanothallite (Cu_2OCl_2) is taken from literature (Formica, 1997) (JCPDS Nr. available in the computer software), for the purpose of comparison.

The surface film of copper obtained after immersion in a solution in the absence of inhibitor shows peaks similar to those observed in melanothallite (Cu_2OCl_2).

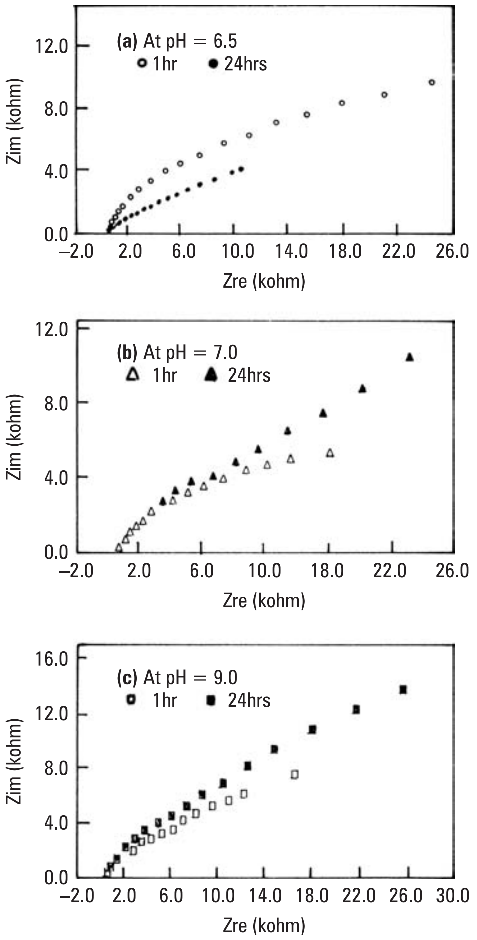
The surface film of copper obtained after immersion in a solution containing the inhibitor exhibited a different pattern from the one that is observed in its absence. The peaks at $2\theta = 36.6^\circ$ and 61.6° due to the product similar to that of Cu_2OCl_2 disappear while the base copper peaks are seen indicating the formation of a protective film on the surface and hence good inhibition efficiency.

Analysis of FTIR spectra

The reflectance absorption FTIR (Hsu, 1997) spectra of a fresh copper plate polished to mirror finish and that of copper immersed in an aqueous environment containing 300 ppm chloride in the absence and presence of inhibitor are as shown in Figures 8, 9 and 10 respectively. The period of immersion is ten days.

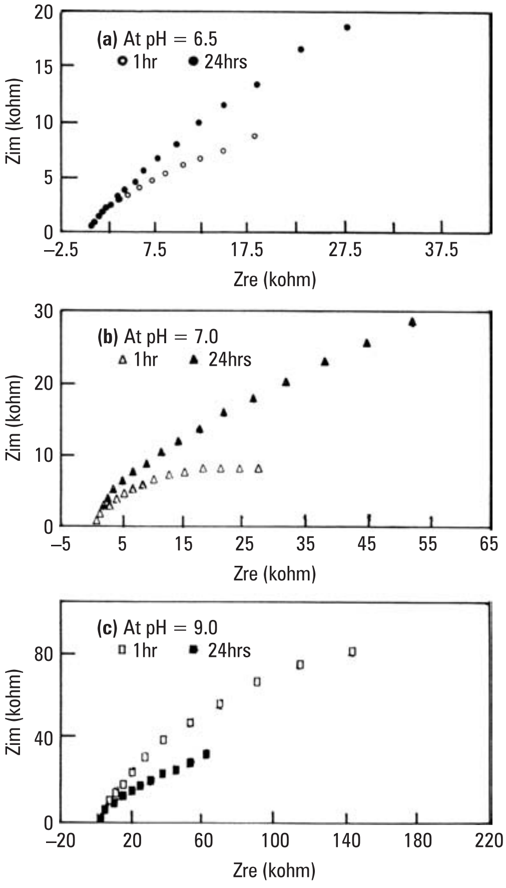
As expected, the mirror finished surface exhibits hardly any IR pattern. The noise like low intense pattern is due to the time-averaged differential aerial absorption during

Figure 3 AC-impedance curves in absence of inhibitor



A.C. Impedance curves of copper immersed in an aqueous environment containing 300 ppm chloride and at various pH values in the absence of the inhibitor after one hour and 24 hours immersion periods

Figure 4 AC-impedance curves in presence of 20ppm inhibitor



A.C. Impedance curves of copper immersed in an aqueous environment containing 300 ppm chloride and at various pH values in the presence of the inhibitor (20 ppm), 5-mercapto-3-p-nitrophenyl 1,2,4 triazole after one hour and 24 hours immersion periods

the duration of measurement. However, the copper plate exposed to the chloride environment for ten days in the absence of inhibitor shows a heavy absorption from 4,500cm^{-1} to 1,600cm^{-1} due to Cu-O-Cu-O skeletal vibrations and at 600cm^{-1} due to Cu-O stretching. This is a typical IR pattern for the corroded copper surface. The reflectance absorption IR spectrum of the copper plate exposed to a similar solution in the presence of 20 ppm of the organic inhibitor is nearly identical to that of the polished copper surface. This supports the idea that the copper surface is protected by the formation of a protective film involving the copper surface and the ligand. The absence of any peaks of the ligand origin in this spectrum is not unusual because the surface film is perhaps of a molecular thickness and the IR spectroscopy is not that sensitive to detect bands of a single molecule.

Analysis of ESCA spectra

The ESCA patterns of the protective films formed on copper surface immersed in neutral aqueous environment containing 300 ppm chloride in the absence and presence of inhibitor is shown in Figures 11 and 12 respectively.

This ESCA pattern is interpreted with the help of data (Wagner *et al.*, 1978, and literature data taken from the Regional Sophiticated Instrumentation Centre, IIT, Chennai, India) for various elements exhibiting peaks at characteristic binding energy values.

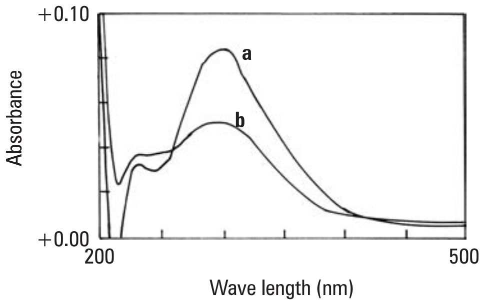
From Figure 12, it is observed that in the presence of the inhibitor, the peak at 70eV corresponds to 3p electrons of copper and the peaks at 932eV and 952eV are due to 2 p electrons of copper. The peak at 199eV is due to 2p electrons of chlorine. The peak at 285eV is due to 1S electron of carbon atom.

Table III Impedance parameters of copper in aqueous environment containing 300 ppm chloride at various values of pH in the absence and presence of inhibitor after one hour and 24 hours immersion periods

Sample no.	Inhibitor conc. ppm	pH	Charge transfer resistance, R_t(k ohm)	Capacitance, C_{dl} (F)	Corrosion Inhibition efficiency, per cent
Immersion period – one hour					
1	0	6.5	3.745	5.68×10^{-5}	-
2	20		29.835	8.40×10^{-5}	87.45
3	0	7.0	14.523	1.04×10^{-4}	-
4	20		131.797	4.37×10^{-5}	88.99
5	0	9.0	13.254	1.04×10^{-5}	-
6	20		171.063	1.87×10^{-5}	92.25
Immersion period – 24 hours					
1	0	6.5	10.331	1.41×10^{-4}	-
2	20		106.876	2.98×10^{-5}	90.34
3	0	7.0	21.336	6.25×10^{-5}	-
4	20		257.988	1.83×10^{-5}	91.73
5	0	9.0	28.808	5.50×10^{-5}	-
6	20		371.063	1.86×10^{-5}	92.24

Notes: Inhibitor system: 5-mercapto-3-p-nitrophenyl-1,2,4-triazole

Figure 5 UV-visible absorption spectra of the solutions in the presence of the inhibitor, 5-mercapto-3-p-nitrophenyl-1,2,4-triazole



(a) Before immersing the copper specimen
(b) After immersing the copper specimen

Figure 6 XRD pattern of the surface film formed on copper immersed in an aqueous environment containing 300 ppm chloride at pH = 7.0 in the absence of the inhibitor

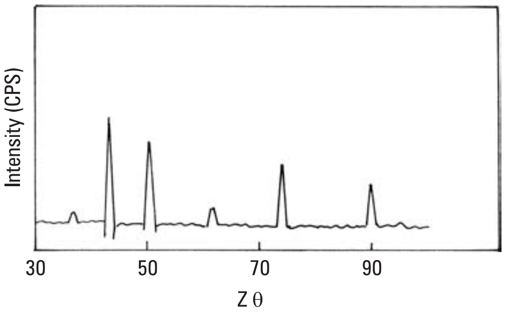


Figure 7 XRD pattern of the surface film formed on copper immersed in an aqueous environment containing 300 ppm chloride at pH = 7.0 in the presence of the inhibitor, 5-mercapto-3-p-nitrophenyl-1,2,4-triazole

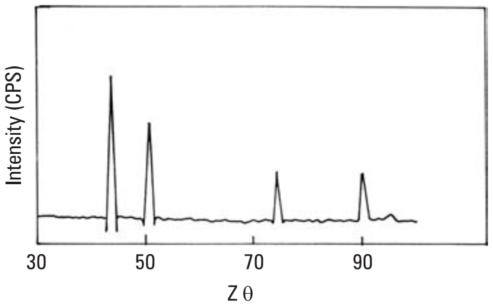


Figure 8 Fourier transform reflectance absorption infrared spectrum of a fresh copper plate polished to mirror finish

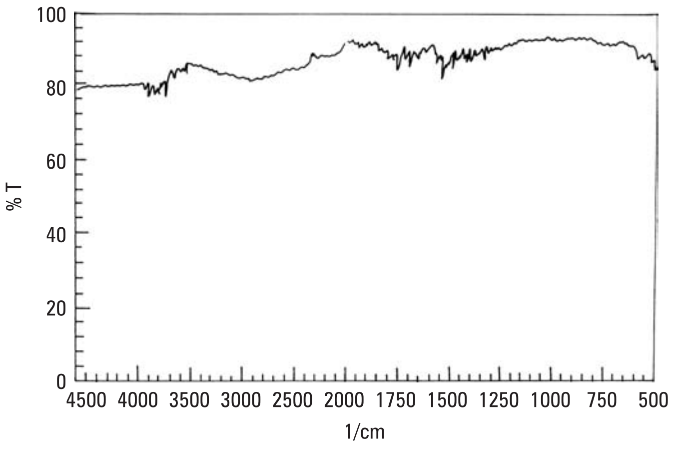


Figure 9 Fourier transform reflectance absorption infrared spectrum of the surface film formed on copper immersed in an aqueous environment containing 300 ppm chloride in the absence of the inhibitor

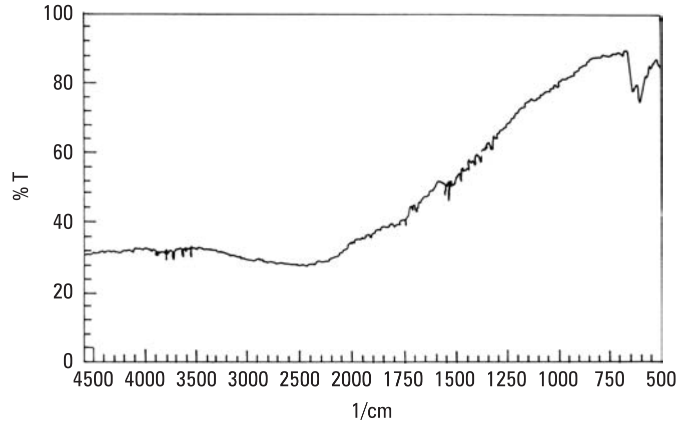
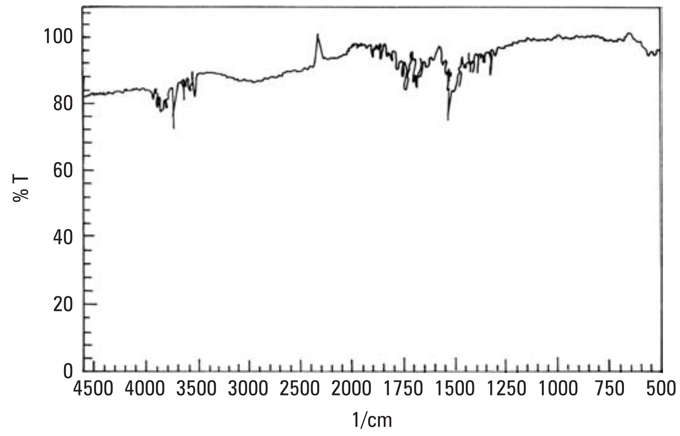


Figure 10 Fourier transform reflectance absorption infrared spectrum of the surface film formed on copper immersed in an aqueous environment containing 300 ppm chloride in the presence of the inhibitor, 5-mercapto-3-p-nitrophenyl-1,2,3-triazole



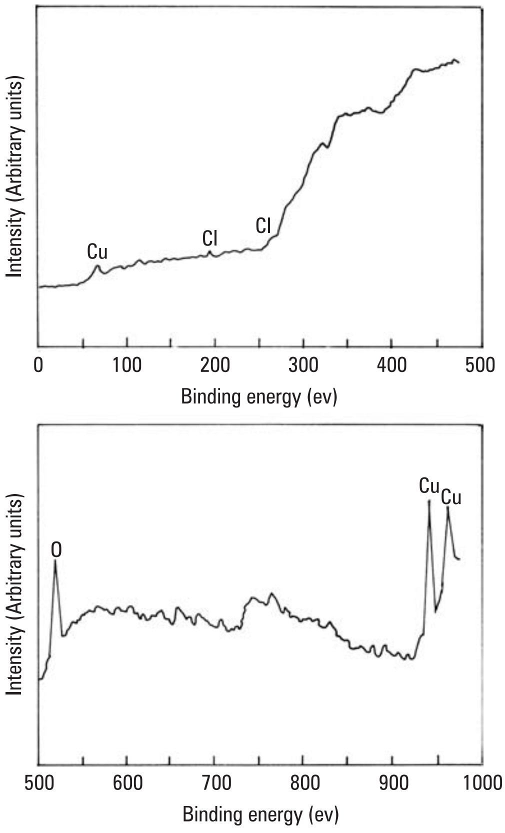
The observed peak at 162eV is due to 2p electrons of sulphur atom. The peak at 401eV is due to 1S electron of nitrogen atom. The peak at 530eV is due to 1S electron of oxygen atom from NO_2 group of the ligand.

Mechanism of inhibition of corrosion

The results of weight loss method reveal that this system has maximum inhibition efficiency in the range of 92 to 94 per cent at 15 ppm of the inhibitor concentration at various concentrations of chloride ranging from 50 to 300 ppm at neutral pH.

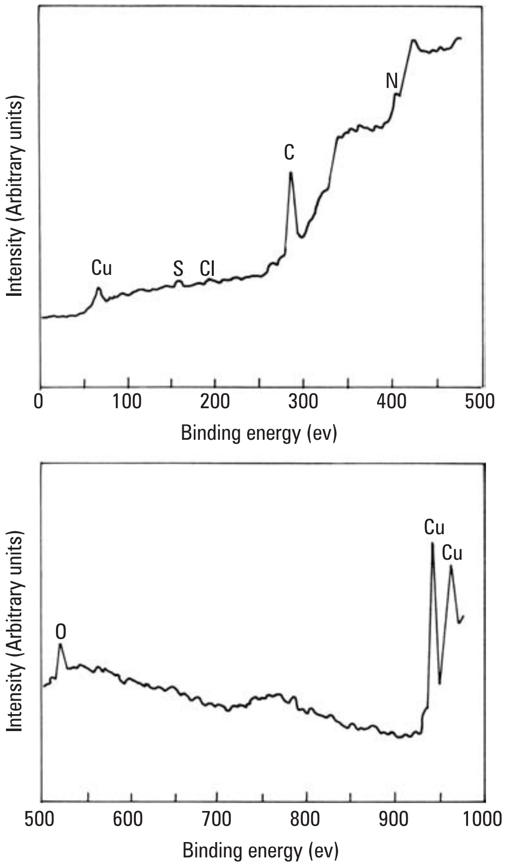
The polarisation studies show that this compound acts as a mixed inhibitor, though there is variation depending upon the pH, whether it is predominantly controlling the cathodic reaction or anodic reaction. The UV-visible absorption spectra of the solutions containing the inhibitor after the immersion of the copper specimen indicate the formation of a soluble complex in solution to a very small extent, which must be before the formation of a protective film on the copper surface.

Figure 11 ESCA pattern of the surface film formed on copper immersed in an aqueous environment containing 300 ppm chloride at neutral pH in the absence of the inhibitor



The X-ray diffraction studies and the FTIR studies suggest the absence of any oxide or chloride in the protective film. However, ESCA patterns clearly reveal the presence of chloride on the copper surface but not oxygen (of any oxide film). As the film is very thin, the presence of chloride could not be detected by the XRD technique. The protective film appears to be transparent and extremely thin. All the above experimental results suggest that there is a presence of chloride ion in the protective film on the copper surface. All the elements that are present in the inhibitor molecules are also present in the protective

Figure 12 ESCA pattern of the surface film formed on copper immersed in an aqueous environment containing 300 ppm chloride at neutral pH in the presence of the inhibitor, 5-mercapto-3-p-nitrophenyl-1,2,4-triazole



film. In other words, the protective film consists of cuprous chloride, CuCl or $CuCl_2^-$ complex ion or both and also the Cu (I) – inhibitor complex. There is no cuprous oxide or any oxide of copper in the protective film. In order to explain all these observations, in a holistic way, the following mechanism of inhibition of corrosion has been proposed.

The anodic dissolution mechanism of copper in the presence of the inhibitor in neutral and alkaline aqueous environment containing chlorides in the presence of oxygen is as follows:

$Cu \longrightarrow Cu^+ + e^-$
$Cu^+ + Cl^- \longrightarrow CuCl$
$CuCl + Cl^- \longrightarrow CuCl_2^-$

The role and action of the inhibitor involve the following steps:

1. The first step involves the diffusion of the inhibitor from the bulk to the copper surface because of the concentration gradient between the bulk of the solution and the surface of the metal.
2. The second step involves the chemisorption of the inhibitor molecules on the surface of the copper.
3. In the third stage, the surface reaction takes place at the anodic sites between copper ions and the chemisorbed inhibitor molecules involving the formation of copper (I) – inhibitor insoluble complex which is very thin, may be of unimolecular thickness. On the cathodic sites, the inhibitor molecules are simply chemisorbed. It acts as a protection film and prevents further corrosion.
4. Once the protective film is formed, the anodic dissolution is prevented and the diffusion of oxygen to the surface is also prevented thus controlling both the anodic and cathodic reactions. It shows that the system is mostly acting as a mixed inhibitor.
5. Thus the protective film consists of cuprous chloride, CuCl or $CuCl_2^-$ complex ion or both and also the Cu (I) – inhibitor complex.

Conclusions

The following points are concluded.

1. A maximum corrosion inhibition efficiency of 92.75 per cent is obtained by 5-mercapto-3-p-nitrophenyl-1,2,4-triazole at 15 ppm of inhibitor concentration in 300 ppm chloride at neutral pH.
2. The inhibition efficiency of the system ranges from 81.89 and 96.99 per cent in the pH range 6.5-9.0. This inhibitor is very much effective in the pH range 6.5-9.0. and less effective at pH = 6.0 with an efficiency of only 60.01 per cent.
3. At pH = 7.0, it acts as a mixed inhibitor predominantly controlling the cathodic reaction.
4. The protective surface film consists of copper (I)-5-mercapto-3-p-nitrophenyl-1,2,4-triazole complex and cuprous chloride and does not consist of any oxide of copper.

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