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Studies on triazole derivatives as inhibitors for the corrosion of muntz metal in acidic and neutral solutions

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Abstract

The influence of few triazole derivatives namely, 4-amino-5-mercapto-3-methyl 1,2,4 triazole (AMMT), 4-amino-5-mercapto-3-methyl 1,2,4 triazole (AMET) and 4-amino-5-mercapto-3-propyl 1,2,4 triazole (AMPT) on the corrosion behavior of muntz metal (60Cu–40Zn) in acidic and neutral solutions has been studied using weight loss measurements and potentiodynamic polarization methods. Surface morphological examinations such as UV spectral analysis, XRD and SEM have also been carried out to understand the mechanism of inhibition of corrosion. All the triazoles derivatives are found to inhibit the corrosion of muntz metal very effectively in both the acidic and neutral solutions. Polarization measurements clearly show that the inhibitors behave as mixed type in neutral medium and are predominantly cathodic nature in acidic solutions. UV spectra, XRD and Scanning Electron Microscopic studies clearly reveal the formation of a strongly adsorbed film on the metal surface, which is responsible for the inhibition of corrosion in both the media. From the above studies, it can be concluded that the inhibition of corrosion by these compounds is due to a chmisorption process. Among these compounds, AMPT is found to offer better corrosion inhibition than the other compounds.

Keywords: Alloys; Corrosion; Triazole derivatives; X-ray crystallography; Surface morphological studies

1. Introduction

Heterocyclic compounds containing sulphur nitrogen and oxygen especially triazoles have been serving as very effective inhibitors for the corrosion of metals and alloys in different corrosive environments [1–3]. Triazoles as inhibitors have been studied for the protection of copper and copper based alloys in different corrosive environments [4–7]. Copper and copper based alloys are widely used in the construction of heat exchangers, condensers and fluid control devices. They are also used in architectural items, building fronts, rails, lock bodies, doorknobs, electrical wiring, hardware, connectors, printed circuit boards and electronic applications, etc. To minimize the losses due to corrosion many methods have been developed. Alloying and incorporation of inhibitors have been extensively studied to bring down the corrosion of copper and its alloys in water transport systems [8,9]. Literature survey reveals that a wide variety of organic compounds ranging from long chain aliphatic sulphides to benzene derivatives containing nitrogen or sulphur have been found to be effective inhibitors for the corrosion of copper and copper alloys [10]. Still a thorough knowledge is needed on newly synthesized triazole derivatives especially on the corrosion behavior of copper based alloys. The present study aims at the influence of triazole derivatives such as 4-amino-5-mercapto-3-methyl 1,2,4 triazole (AMMT), 4-amino-5-mercapto-3-methyl 1,2,4 triazole (AMET) and 4-amino-5-mercapto-3-propyl 1,2,4 triazole (AMPT) on the inhibition of corrosion of muntz metal in 1N HCl and 3.5% NaCl using weight loss, electrochemical methods and surface characterization studies.

2. Experimental

Muntz metal of composition Cu-60% and Zn-40% were used for all the studies. Specimens of size 5 cm × 2 cm × 0.25 cm were used for weight loss measurements. An electrode of 1 cm^2 area was used for potentiodynamic polarization studies. The electrode was polished to obtain a smooth fine surface using different grades of emery paper and then degreased with trichloroethylene. AR grade reagents such as HCl and NaCl were used for preparing all solutions. The

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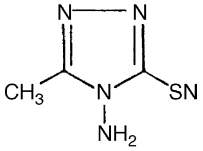
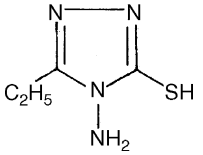
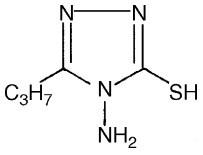
Table 1
Molecular formula and structures of inhibitors

Compound name	Structure	Molecular formula
AMMT		$C_3H_6N_4S$
AMET		$C_4H_8N_4S$
AMPT		$C_5H_{10}N_4S$

inhibitors were synthesized in the laboratory as per procedure reported else were [11]. Structural formulae of triazole derivatives used in this study are shown in Table 1. Both weight loss and potentiodynamic polarization studies were carried out as described elsewhere [12]. Polarization curves were recorded using a three-electrode electrochemical cell, measuring through, BAS Model 10 A computerized electrochemical analyzer. A platinum foil and a calomel electrode were used as auxiliary and reference electrode respectively. The surfaces of corroded and inhibited specimens were examined by UV spectral reflectance measurements using U-3400 Spectrometer (UV–VIS–NIR Spectrometer, Hitachi, Japan) and Scanning electron microscopic studies (Scanning Electron Microscopy JEOL (JSM −35CF). Corrosion products adhering to the surface were examined by X-ray diffractometry (Model JEOL 8030) using Cu Kα (λ = 1.541 Å) as a target material.

3. Results and discussion

3.1. Weight loss measurements

Table 2 shows the values of inhibition efficiency for the corrosion of muntz metal in 1N HCl and 3.5% NaCl solution in the presence of different concentrations of triazole derivatives. It can be seen from the table that these compounds inhibit corrosion of muntz metal even at a very low concentration in both the media. Inhibition efficiencies of these compounds are found to be high, when the concentrations of inhibitors are found to be 500 ppm and beyond this concentration it is slightly less effective. It is seen that that the inhibition is due to the π-electrons, contributed from the different anchoring atoms of the molecule. By observing the molecular structure of these compounds, the molecules are absorbed on the metal surface through N and S atoms, –N=CH groups and aromatic rings [13,14]. Moreover, the presence of OH and chloride ions increases the solubility of organic compounds in aqueous medium, which enables the prevention of the materials. In acidic solutions, the formation of protonated species takes place which leads to the electrostatic interaction between these species and the negatively charged metal surface [15,16]. The inhibition efficiency is found to be more than 90% for 700 ppm of the inhibitor concentration. It

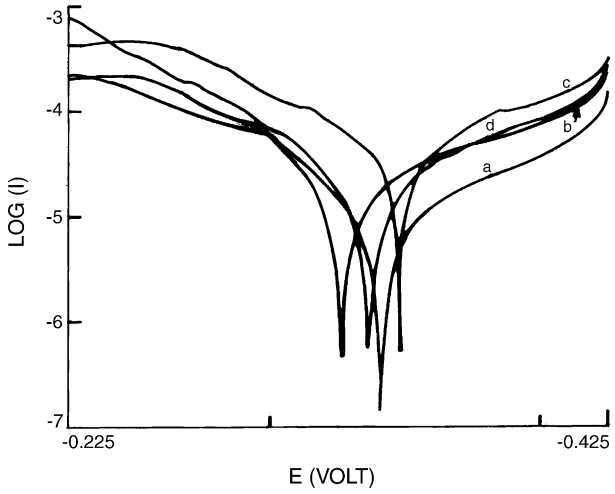


Fig. 1. Potentiodynamic polarization curves for muntz metal in 3.5% NaCl containing different concentrations of AMMT: (a) NaCl alone, (b) 100 ppm, (c) 300 ppm and (d) 600 ppm.

is mainly due to the formation of a stable adsorbed film on the metal surface. It is attributed due to the chemisorption of the compound by interaction between the loan pair of electrons of nitrogen atoms and the positively charged metal surface [17]. The values of inhibition efficiency obtained by these compounds follow the order AMPT > AMET > AMMT. It has been reported that the efficiency of an inhibitor improves with the increase in the polarity of the substitutent and the electron acceptor characteristics of compounds by the introduction of electron donating group [18,19].

3.2. Potentiodynamic polarization studies

The anodic and cathodic polarization curves for muntz metal in 3.5% NaCl and 1 M HCl in absence and presence of different concentrations of triazole derivatives are shown in Figs. 1–6. The

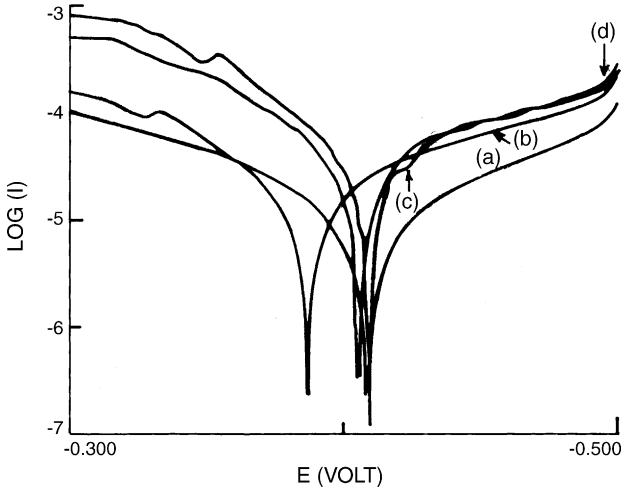


Fig. 2. Potentiodynamic polarization curves for muntz metal in 3.5% NaCl containing different concentrations of AMET: (a) NaCl alone, (b) 100 ppm, (c) 300 ppm and (d) 600 ppm.

Table 2
Values of inhibition efficiency for different concentrations of triazole from weight loss measurement

Sl. no.	Concentration of the inhibitor (ppm)	Inhibition efficiency (%)					
		1N HCl			3.5% NaCl		
		AMMT	AMET	AMPT	AMMT	AMET	AMPT
1	50	32.8	34.0	35.5	31.2	33.4	34.2
2	100	64.2	66.5	68.1	68.4	70.2	72.5
3	200	70.6	71.2	72.0	73.5	74.1	76.7
4	300	75.2	76.7	77.9	77.4	82.6	83.5
5	400	78.4	81.2	82.2	79.2	85.5	86.7
6	500	81.5	84.6	86.7	80.1	87.2	89.4
7	600	86.4	87.2	88.5	83.5	91.2	93.1
8	700	89.1	90.1	92.0	93.0	94.4	96.6

Table 3
Corrosion kinetic parameters for the corrosion of muntz metal in 1N HCl and 3.5% NaCl in the presence of different concentrations of triazoles

Sl. no.	1N HCl						3.5% NaCl					
	Inhibitor concentration (ppm)	E_{corr} (mV)	Tafel slopes (mV dec^{-1})		$I_{corr} \propto A$ (cm^{-2})	I.E. (%)	Inhibitor concentration (ppm)	E_{corr} (mv)	Tafel slopes (mV dec^{-1})		$I_{corr} \propto A$ (cm^{-2})	I.E. (%)
			b_a	b_c					b_a	b_c		
1	1N HCl	−360	85	134	17.2	–	3.5% NaCl	−355	65.2	104.2	5.8	–
2	50 AMMT	−358	87	141	11.4	33.7	50 AMMT	−352	67.6	106.4	3.9	32.7
3	100 AMMT	−355	88	145	6.0	65.1	100 AMMT	−347	69.2	109.6	1.6	72.4
4	300 AMMT	−352	92	153	4.0	76.7	300 AMMT	−345	72.4	111.2	1.1	81.1
5	600 AMMT	−348	95	162	2.2	87.2	600 AMMT	−342	76.2	114.3	0.8	86.2
6	50 AMET	−356	87	146	11.2	34.8	50 AMET	−352	66.4	107.8	3.8	34.4
7	100 AMET	−352	89	156	5.6	67.5	100 AMET	−345	68.6	109.2	1.4	75.8
8	300 AMET	−347	93	164	3.7	78.5	300 AMET	−343	73.2	113.6	0.9	84.5
9	600 AMET	−345	96	170	2.0	88.4	600 AMET	−340	76.9	116.8	0.5	91.4
10	50 AMPT	−353	90	148	11.0	36.0	50 AMPT	−348	68.0	108.2	3.7	36.2
11	100 AMPT	−349	92	157	5.4	68.6	100 AMPT	−346	69.6	111.4	1.2	79.3
12	300 AMPT	−345	94	165	3.5	79.6	300 AMPT	−341	74.4	115.5	0.8	86.2
13	600 AMPT	−343	98	172	1.8	89.5	600 AMPT	−336	78.2	119.2	0.4	93.1

Table 4
Corrosion parameters for the corrosion of muntz metal in 3.5% NaCl at different temperatures in presence of triazole derivatives (600 ppm)

Sl. no.	Temperature	NaCl alone		3.5% NaCl + AMMT			3.5% NaCl + AMET			3.5% NaCl + AMPT		
		E_{corr} (MV)	$I_{corr} \propto A$ (cm^{-2})	E_{corr} (mV)	$I_{corr} \propto A$ (cm^{-2})	I.E. (%)	E_{corr} (mV)	$I_{corr} \propto A$ (cm^{-2})	I.E. (%)	E_{corr} (mV)	$I_{corr} \propto A$ (cm^{-2})	I.E. (%)
1	30	−355	5.8	−316	0.8	86.2	−314	0.5	91.3	−310	0.4	93.1
2	50	−375	7.2	−322	1.7	70.6	−320	0.9	84.5	−326	0.75	87.0
3	70	−417	8.2	−326	2.9	50.0	−324	2.7	53.4	−331	2.5	56.8
4	90	−454	9.7	−336	3.2	44.8	−329	2.9	50.0	−336	2.8	51.7

Table 5
Corrosion parameters for the corrosion of muntz metal in IN HCl at different temperatures in presence of triazole derivatives (600 ppm)

Sl. no.	Temperature	HCl alone		IN HCL + AMMT			IN HCl + AMET			IN HCl + AMPT		
		E_{corr} (MV)	$I_{corr} \propto A$ (cm^{-2})	E_{corr} (mV)	$I_{corr} \propto A$ (cm^{-2})	I.E. (%)	E_{corr} (mV)	$I_{corr} \propto A$ (cm^{-2})	I.E. (%)	E_{corr} (mV)	$I_{corr} \propto A$ (cm^{-2})	I.E. (%)
1	30	−360	17.2	−348	2.2	87.2	−345	2.0	88.4	−343	1.8	89.5
2	50	−372	14.9	−356	4.0	76.7	−352	4.2	75.5	−348	3.8	77.9
3	70	−381	18.9	−362	6.1	64.5	−364	5.8	66.2	−363	5.7	66.8
4	90	−415	21.8	−376	8.2	52.3	−378	7.9	54.0	−382	7.4	56.9

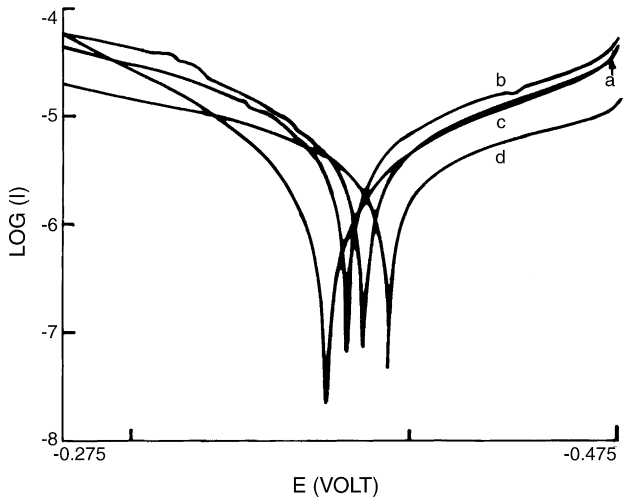


Fig. 3. Potentiodynamic polarization curves for muntz metal in 3.5% NaCl containing different concentrations of AMPT: (a) NaCl alone, (b) 100 ppm, (c) 300 ppm and (d) 600 ppm.

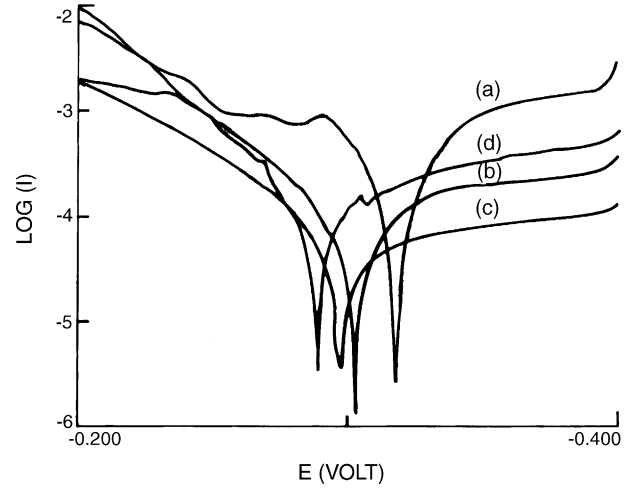


Fig. 4. Potentiodynamic polarization curves for muntz metal in 1N HCl containing different concentrations of AMMT: (a) HCl alone, (b) 100 ppm, (c) 300 ppm and (d) 600 ppm.

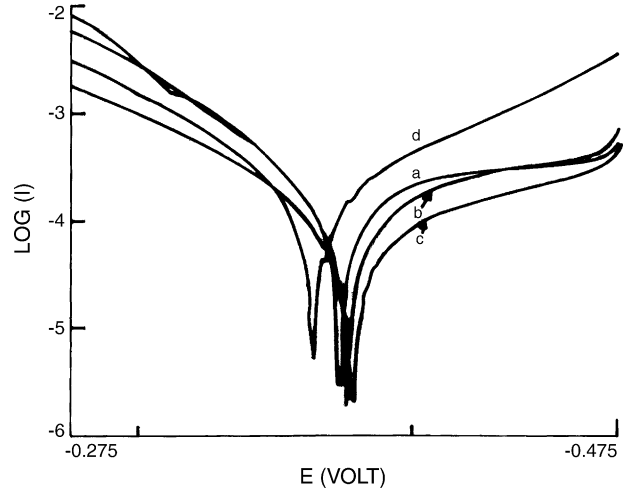


Fig. 5. Potentiodynamic polarization curves for muntz metal in 1N HCl containing different concentrations of AMET: (a) HCl alone, (b) 100 ppm, (c) 300 ppm and (d) 600 ppm.

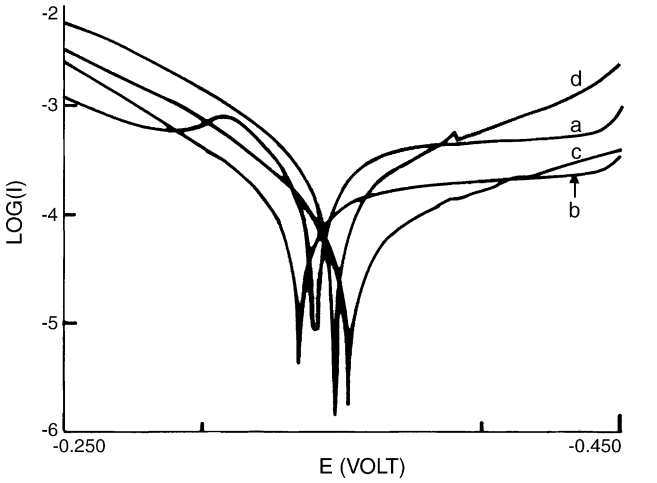


Fig. 6. Potentiodynamic polarization curves for muntz metal in 1N HCl containing different concentrations of AMPT: (a) HCl alone, (b) 100 ppm, (c) 300 ppm and (d) 600 ppm.

corrosion kinetic parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}) and Tafel slopes (b_a and b_c) derived from potentiodynamic polarization curves are given in Table 3. The polarization curves have also been recorded at different temperatures ranging from 30 to 90 °C in the presence of optimum concentration of 600 ppm of triazole derivatives and the values are presented in Tables 4 and 5. The values of corrosion potential (E_{corr}) for different concentrations of acid and neutral media reveal that there is a shift in corrosion potential to less negative values with reference to the blank solution. In both the media, it is noted that the shift in potential towards more negative values with respect to increase in temperature. This observation depicts that the rate of corrosion increases with increase in temperature. It may be due to the desorption process of the adsorbed inhibitor occurs more quickly at higher temperature. According to Putilova et al. [20], the behavior of these compounds can be compared to the unstable catalyst poisons whose adsorption falls appreciably with increase in temperature. An increase in concentration of inhibitor in test solution shifts the E_{corr} values towards more anodic direction, which indicates that, the formation of a protective layer on the metal surface. The above observation shows that the inhibitors are more effective in both the media and does not show any characteristic protective film at higher temperatures.

Values of I_{corr} are obtained by the extrapolation of Tafel values in both the media in the presence and absence of triazole derivatives reveal that the self corrosion is more in HCl than in NaCl solution. All these compounds are found to bring down the extent of corrosion in both the media threby serving as effective corrosion inhibitors. But AMPT is found to be more effective than AMET and AMMT. The order of efficiencies in both the media can be written as:

AMPT > AMET > AMMT

This order is found to be similar to that of the values of corrosion inhibition efficiencies obtained from weight loss measurements. The inhibitor AMPT is found to be more effective

because of the presence of a large molecular area of the compound and greater electron releasing ability (+I effect) of the propyl group present in it. It is also observed that the increase in temperature gradually enhances the corrosion rate by desorption of the barrier layers on the surface of the metal. This may be due to the fact that at higher temperature the metal organic complex layer dissociates leaving a porous diffused film, which is responsible for the corrosion of metal. In the absence of triazole compounds in acidic medium, the cathodic and anodic Tafel slopes are found to be 134 and 85 mV dec^{-1}, respectively. Similarly in the case of neutral solutions b_a and b_c values are found to be 104 and 65 mV dec^{-1}, respectively. These values are good agreement with the reported datas [19,20]. The increase in concentration of inhibitors influence the b_a and b_c values to an equal extent in neutral medium which emphasizes that the compound act as a mixed type inhibitor. Whereas in the case of acid medium, the cathodic slope is found to increase more, which indicates that it, act as predominantly as cathodic inhibitor.

3.3. Surface morphological studies

SEM photographs for muntz metal obtained for both the media in presence of 600 ppm of AMPT is shown in Fig. 7(a and b). It shows that the formation of a thick adsorbed film on the metal surface, which is responsible for the inhibition of corrosion. The protective film is found to be more thicker in the case of HCl solution than in NaCl solution.

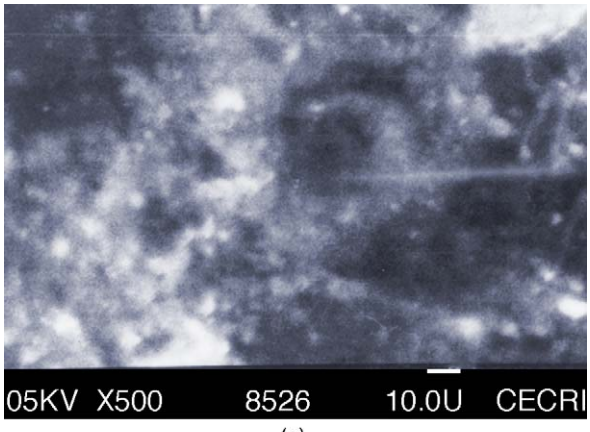


Fig. 7. SEM photograph for muntz metal in (a) 3.5% NaCl and (b) 1N HCl in the presence of 600 ppm of AMPT.

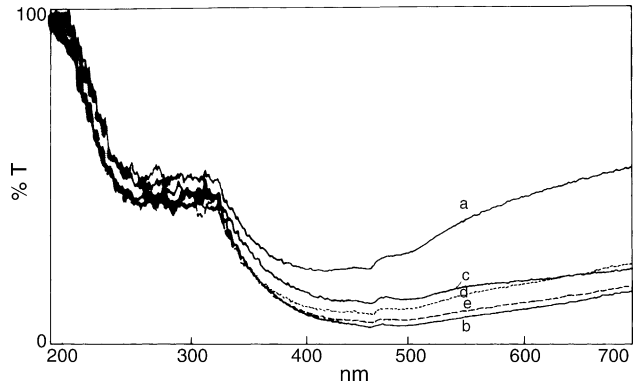


Fig. 8. UV reflectance spectra for muntz metal in 3.5% NaCl in the presence of triazole derivatives. (a) Polished metal, (b) polished metal immersed in 3.5% NaCl, (c) 3.5% NaCl containing 600 ppm of AMMT, (d) 3.5% NaCl containing 600 ppm of AMET and (e). 3.5% NaCl containing 600 ppm of AMPT.

UV reflectance spectra were obtained for muntz metal as polished and tested in corrosive media and in the presence and absence of 600 ppm of AMMT, AMET and AMPT are shown in Figs. 8 and 9. It can be observed that the percentage of reflectance is maximum for polished specimen and found to decrease considerably in the case of specimens dipped in corrosive media. This observation clearly reveals that the change of surface characteristics due to the corrosion of the metal in acidic and neutral solutions. In presence of triazole derivatives the percentage of reflectance gets reduced. This attributes that the surface characteristics are not much altered and it may be due to the formation of strongly, adsorbed film on the metal surface.

XRD patterns recorded before and after corrosion of muntz metal both in the presence and absence of triazole derivatives are shown in Fig. 10. The spectrum for as polished specimens shows the characteristic lines of Cu and Zn and the intensity of

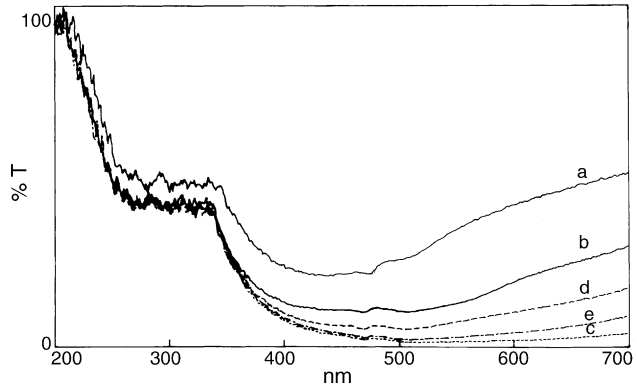


Fig. 9. UV reflectance spectra for muntz metal in 1N HCl in the presence of triazole derivatives. (a) Polished metal, (b) polished metal immersed in 1N HCl, (c) 1N HCl containing 600 ppm of AMMT, (d) 1N HCl containing 600 ppm of AMET and (e) 1N HCl containing 600 ppm of AMPT.

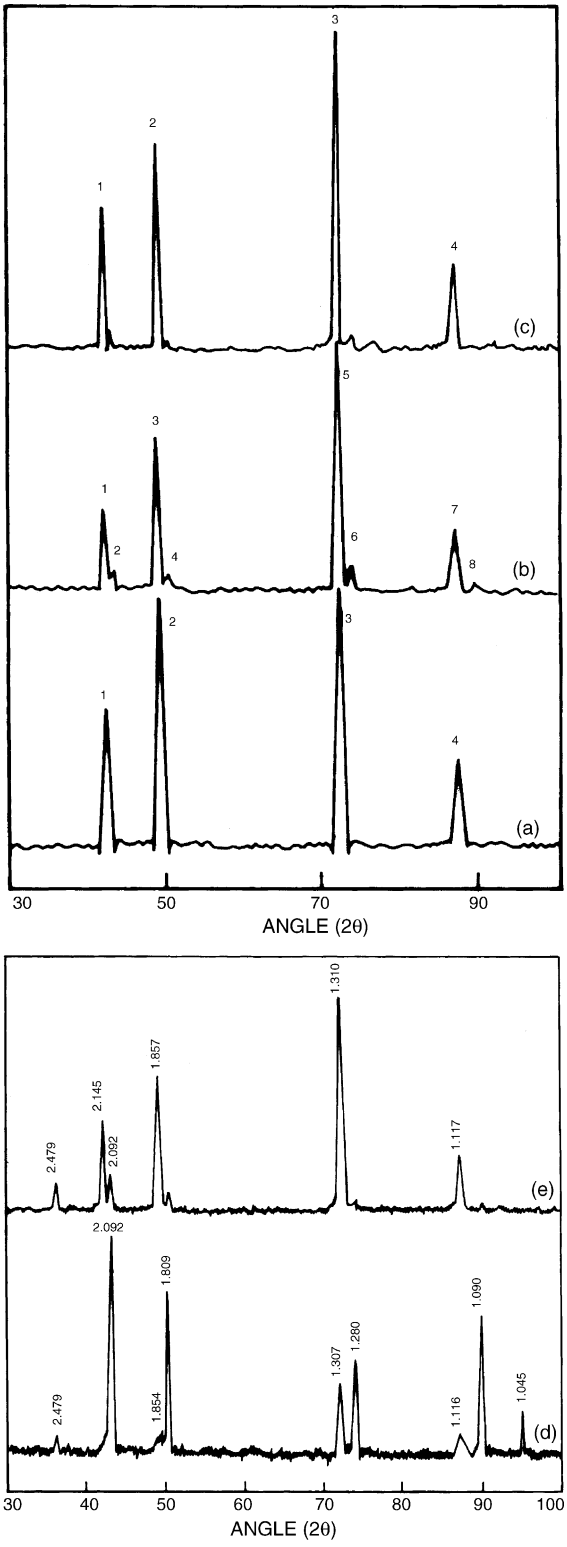


Fig. 10. XRD spectrum of muntz metal (a) polished metal, (b) polished metal immersed in 3.5% NaCl, (c) 3.5% NaCl containing 600 ppm of AMPT, (d) polished metal immersed in 1N HCl and (e) 1N HCl containing 600 ppm of AMPT.

such lines are well above the background fluorescent intensity. XRD spectrum of muntz metal dipped in 1 M HCl shows that the appearance of many peaks, which shows the presence of oxides such as cuprous oxide, cupric chloride in the corrosion product. In the presence of AMPT, shows the absence of many peaks, which indicates a thin impervious metal organic complex layer on the metal surface. Similar observations have been made in the case of NaCl solution in the presence of inhibitor compounds.

4. Conclusions

Triazoles inhibit the corrosion of muntz metal to almost an equal extent in both the media in the order of AMPT > AMET > AMMT. The inhibition of corrosion of muntz metal in the presence of triazoles is under cathodic control in 1N HCl and in 3.5% NaCl it is found to be mixed control. The inhibition of corrosion of muntz metal in both the media by triazole derivatives may be due to the formation of a thick adsorbed and impervious protective film, which has been confirmed by surface morphological studies.

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