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5-(3-Aminophenyl)tetrazole – A new corrosion inhibitor for Cu–Ni (90/10) alloy in seawater and sulphide containing seawater

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Abstract The inhibition performance of 5-(3-aminophenyl)tetrazole (APT) in controlling corrosion of Cu–Ni (90/10) alloy in synthetic seawater and synthetic seawater containing 10 ppm sulphide has been investigated. Electrochemical impedance, potentiodynamic polarization, cyclic voltammetry (CV) weight-loss and scanning electron microscopy (SEM)/energy dispersive X-ray analysis (EDX) studies were employed to evaluate the inhibitor performance. The results of impedance studies show that both charge transfer resistance and film resistance increase with an increase in APT concentration and at a concentration of 6.5 mM, APT functions as an excellent inhibitor with an inhibition efficiency of 99.72%. The phase angle Bode plots are more broadened and showed a phase maximum of 81° in the presence of APT. The APT film is highly protective even at a temperature of 60 °C. Potentiodynamic polarization studies inferred that APT functions as a mixed inhibitor. CV studies revealed that the protective APT film is stable even up to anodic potentials of +850 mV vs. Ag/AgCl. Weight-loss studies showed an inhibition efficiency of more than 99% in the presence of APT even after 30 days immersion period. SEM–EDX studies confirm the absence of any corrosion and presence of protective APT film on the alloy surface.

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1. Introduction

Cu–Ni (90/10) alloy has been used for many years as a construction material for seawater piping, heat exchangers and condensers in ships, desalination plants, power plants, ship hulls etc. This extensive use has triggered numerous investigations of this alloy with the aim of improving their performance under various conditions (Beccaria and Crousier, 1989; Blundy and Pryor, 1972; Shih and Pickering, 1987; Hack and Pickering, 1991; Kato et al., 1980). This alloy is resistant to stress corrosion cracking by ammonia and sulphide ions (Powell, 1998) and has good resistance to biofouling due to

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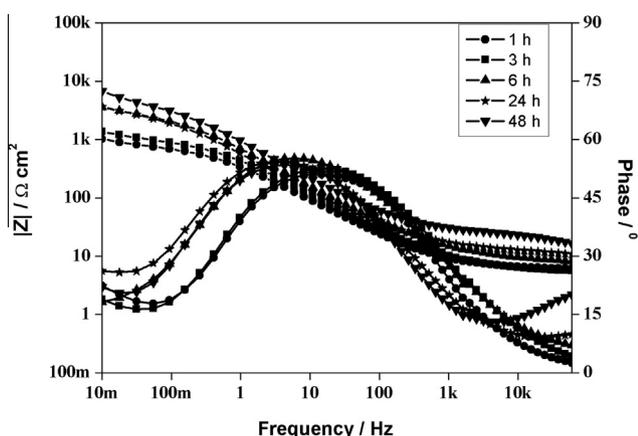
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Table 1 Composition of the Cu–Ni (90/10) alloy.

Element	Cu	Ni	Fe	Mn	Pb	Al	Others in trace amounts
Composition (wt%)	88.512	9.882	1.086	0.412	0.046	0.038	0.024

Table 2 Composition of the synthetic seawater.

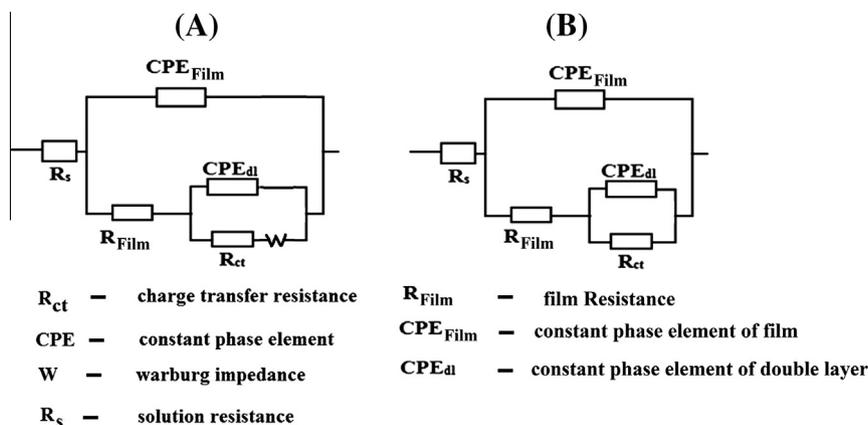
Compound name	NaCl	KCl	MgCl ₂ .6H ₂ O	CaCl ₂	MgSO ₄ .7H ₂ O	NaHCO ₃	KBr	H ₃ BO ₃	SrCl ₂ .6H ₂ O	NaF
g L ⁻¹	27.24	1.40	10.11	2.28	13.92	0.39	0.20	0.026	0.04	0.006

**Figure 1** Bode plots of Cu–Ni (90/10) alloy in synthetic seawater at different immersion periods. [Temperature: 30 °C].

the release of copper ions (Mansfeld and Little, 1992; Hall and Barker, 1985). This alloy is also resistant to pitting and crevice corrosion in quiet seawater (Kato et al., 1980). The corrosion resistance of this alloy is correlated to the performance of the passive film, which is mainly composed of Cu₂O (Cere and Vazquez, 2002; Bockris et al., 1972), though the other copper (II) based compounds such as atacamite and cupric oxide are also present in the film after long exposure (Hall and Barker, 1985). The cupric species generally overlies the cuprous species (Little et al., 1991; Tuthill, 1987). Nevertheless, in the presence of sulphide ions in the environment, the corrosion rate of Cu–Ni (90/10) alloy increases due to the formation of a non-protective layer containing sulphide (Mor and Beccaria, 1975; Syrett, 1981; Eiselstein et al., 1983). The pollution of the seawater by sulphide results in the formation of a contaminated surface film which has better electrocatalytic properties for oxygen reduction than the cuprous oxide films formed in clean aerated seawater (De Sanchezis and Schiffrin, 1982).

Table 3 Impedance parameters of Cu–Ni (90/10) alloy in seawater at different immersion periods. (Temperature: 30 °C).

Immersion period (h)	R_{ct} (kΩ cm ²)	C_{dl} (μF cm ⁻²)	n_1	R_{film} (kΩ cm ²)	C_{film} (μF cm ⁻²)	n_2	Error (%)
1	0.722	28.41	0.64	0.002	36.44	0.60	0.4
3	1.004	14.50	0.65	0.005	34.81	0.64	0.6
6	3.168	13.30	0.66	0.007	27.34	0.64	0.6
24	4.174	12.32	0.67	0.008	15.47	0.65	0.7
48	4.720	12.20	0.67	0.010	15.12	0.66	0.7

**Figure 2** Equivalent circuits used.

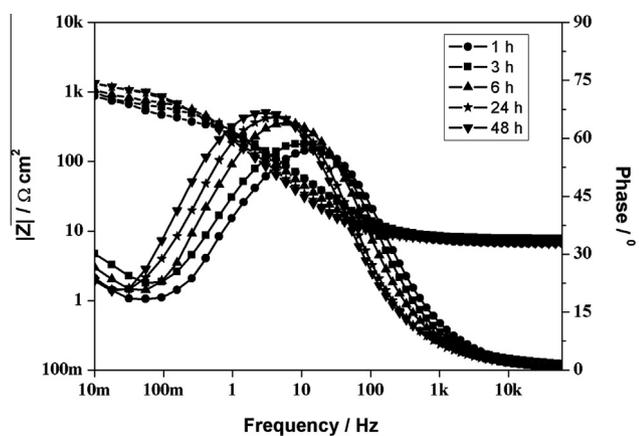


Figure 3 Bode plots of Cu–Ni (90/10) alloy in synthetic seawater containing 10 ppm sulphide at different immersion periods. [Temperature: 30 °C].

The corrosion behaviour of Cu–Ni (90/10) alloy in 3.5% NaCl solution in the absence and presence of sulphide ions was studied by potentiodynamic polarization studies and surface analysis by scanning electron microscopy and X-ray diffraction technique. These studies inferred that the corrosion rate of the alloy increased in the presence of sulphide ions and at a very high concentration of S^{2-} such as 1000 ppm, the alloy suffered from pitting corrosion (Sayed et al., 2003). A very low concentration of 0.01 ppm of S^{2-} is also responsible for corrosion of Cu–Ni (90/10) alloy (Hack, 1980).

Heterocyclic organic compounds such as, azoles were reported to show a marked corrosion inhibition efficiency of Cu–Ni alloys in different corrosive environments (Sutter et al., 1999; Tromans and Hong-Sun, 1991). A few tetrazole derivatives are used as corrosion inhibitors for copper in 0.1 M NaCl environment (Zucchi et al., 1996). 5-Aminotetrazole was used as a corrosion inhibitor for copper in a phosphate electrolyte during electrochemical mechanical planarization (ECMP) of copper (Lee et al., 2005). The inhibiting effect of 5-phenyl-1-H-tetrazole on corrosion of copper in seawater and seawater polluted with thiosulphate or sulphide was studied by using potentiodynamic polarization studies (Al Kharafi et al., 2012). Nevertheless, no studies have been reported in the literature on the corrosion behaviour of Cu–Ni (90/10) alloy in seawater and sulphide-polluted seawater in the presence of 5-(3-aminophenyl) tetrazole as a corrosion inhibitor. A comprehensive study on corrosion inhibition of this alloy in seawater and seawater containing sulphide by 5-(3-aminophenyl)tetrazole has been attempted in the present work. Electrochemical impedance, potentiodynamic polarization, cyclic voltammetry, weight-loss and SEM–EDX studies have been employed.

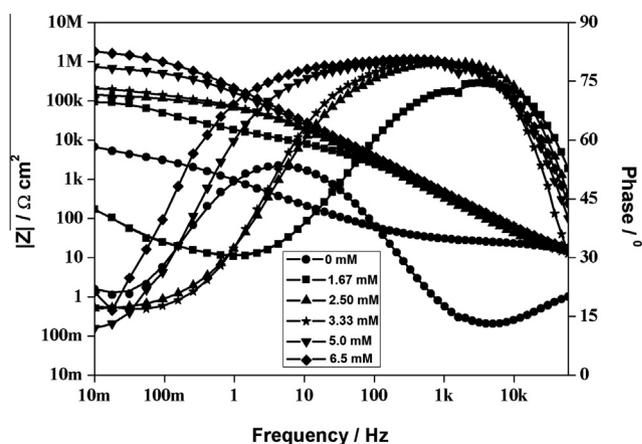


Figure 4 Bode plots of Cu–Ni (90/10) alloy in synthetic seawater in the presence of different concentrations of APT at 48 h immersion period. [Temperature: 30 °C].

2. Experimental

2.1. Materials

The chemical composition of Cu–Ni (90/10) alloy used in the present study is given in Table 1. The composition of the synthetic seawater is given in Table 2 (Yuan and Pehkonen, 2007). All chemicals used in the preparation of synthetic seawater were of AnalaR grade. A stock solution of 1000 ppm of seawater containing sulphide was prepared. From this stock solution, seawater containing 10 ppm sulphide was prepared. 5-(3-aminophenyl)tetrazole (APT) obtained from Sigma–Aldrich Pvt. Ltd., India was used as such. The cupronickel alloy specimens were made from the same Cu–Ni (90/10) alloy sheet. The specimens with the dimensions of $4.0 \times 1.0 \times 0.2$ cm were used for both electrochemical and weight-loss studies. SEM–EDX studies were carried out with the alloy specimens of $0.5 \times 0.5 \times 0.2$ cm. These specimens were polished with 1/0, 2/0, 3/0 and 4/0 grade emery papers consecutively. Later these specimens were polished to mirror finish with alumina and water slurry on a micro polishing cloth, which is fixed on the rotating disc polishing machine. Then, these specimens were washed with triple distilled water, degreased with acetone and dried by blowing N_2 gas for 20 min. In the electrochemical studies, only 1 cm^2 surface area was exposed to the environment and the remaining surface was coated with epoxy resin.

2.2. Electrochemical studies

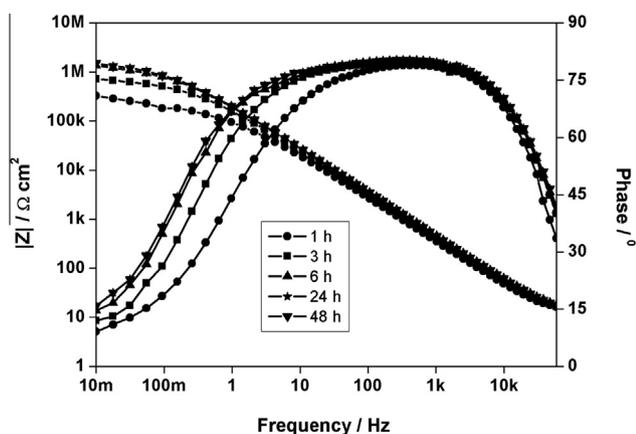
Electrochemical impedance studies were carried out in a three-electrode cell assembly (in accordance with ASTM

Table 4 Impedance parameters of Cu–Ni (90/10) alloy in seawater containing 10 ppm of inorganic sulphide at different immersion periods. (Temperature: 30 °C).

Immersion period (h)	R_{ct} ($k\Omega \text{ cm}^2$)	C_{dl} ($\mu\text{F cm}^{-2}$)	n_1	R_{film} ($k\Omega \text{ cm}^2$)	C_{film} ($\mu\text{F cm}^{-2}$)	n_2	W (DW)	Error (%)
1	0.500	93.02	0.62	0.001	106.5	0.52	161.6	1.1
3	0.512	104.2	0.64	0.002	111.2	0.58	144.7	0.7
6	0.661	161.6	0.64	0.002	174.5	0.60	141.9	0.6
24	0.871	200.2	0.64	0.002	246.7	0.63	131.5	0.9
48	0.992	210.0	0.64	0.003	322.3	0.63	123.6	0.6

Table 5 Impedance parameters of Cu–Ni (90/10) alloy in seawater in the absence and presence of different concentrations of APT at 48 h immersion period. (Temperature: 30 °C).

Concentration of APT (mM)	R_{ct} (k Ω cm 2)	C_{dl} (μ F cm $^{-2}$)	n_1	R_{film} (k Ω cm 2)	C_{film} (μ F cm $^{-2}$)	n_2	Error (%)	IE (%)
0	4.72	12.20	0.67	0.02	15.12	0.66	0.7	–
1.67	19.7	0.420	0.76	6.44	0.552	0.68	1.6	76.04
2.50	167.3	0.387	0.83	44.8	0.398	0.70	0.9	97.18
3.33	238.9	0.214	0.87	221.2	0.284	0.74	0.9	98.02
5.0	491.6	0.077	0.89	342.3	0.150	0.80	0.4	99.04
6.5	1713.0	0.032	0.95	572.3	0.110	0.89	0.6	99.72

**Figure 5** Bode plots of Cu–Ni (90/10) alloy in synthetic seawater in the presence of 6.5 mM APT at different immersion periods. [Temperature: 30 °C].

specifications) with an electrochemical work station; model IM6e Zahner, elektrik, Germany. The Cu–Ni (90/10) alloy was used as the working electrode in the absence and presence of APT in seawater and seawater containing 10 ppm sulphide. A platinum electrode was used as the counter electrode and the reference electrode was Ag/AgCl/1.0 M KCl. The impedance studies were carried out at the open circuit potential (OCP) in the frequency range from 60 kHz to 10 mHz under excitation of sinusoidal wave of ± 5 mV amplitude.

The potentiodynamic polarization studies and cyclic voltammetric studies were carried out by using the same three electrode cell assembly and the electrochemical work station as described under impedance studies. The potentiodynamic polarization studies were conducted in the potential range of -0.7 to $+0.7$ V vs. Ag/AgCl/1.0 M KCl with a scan rate of 1 mV s $^{-1}$. The cyclic voltammetric studies were carried out in the potential range of -1.0 to $+1.0$ V vs. Ag/AgCl/1.0 M KCl with a scan rate of 10 mV s $^{-1}$. All electrochemical studies were conducted at different immersion periods in the range from 1

to 48 h. The impedance studies were carried out at three different temperatures viz. 30, 40 and 60 °C.

2.3. Gravimetric measurements

All gravimetric experiments were carried out in duplicate. The polished Cu–Ni (90/10) alloy specimens were weighed and immersed in 500 mL of seawater in the absence and presence of APT at two different concentrations, for a period of 30 days. Then, these specimens were removed and treated with dilute sulphuric acid (10% by volume) for 3 min at room temperature, in order to remove the corrosion products. Later, these specimens were scrubbed with a bristle brush under running water, degreased with acetone and dried by blowing N $_2$ gas for a period of 20 min. The immersion period of 30 days was fixed in view of the considerable weight-loss obtained in the absence of any inhibitor after this immersion period. During the studies, the difference in the weight-loss of the duplicate specimens immersed in the same solution did not exceed 0.1 mg. Accuracy in weighing was 0.01 mg as recommended by ASTM G31 guidelines (ASTM Standard G 31-72, 1990). Under these conditions, the relative standard error in the determination of corrosion rate is of the order of 2% or less (Freeman and Silverman, 1992). In a similar way, gravimetric studies were performed in seawater containing 10 ppm sulphide also in the absence and presence of APT. Corrosion rates (CR) of the alloy in the absence and presence of APT are expressed in mmpy. Inhibition efficiencies of the inhibitor were calculated by using the formula,

$$IE (\%) = 100 \times \frac{[(CR)_0] - [(CR)_1]}{(CR)_0} \quad (1)$$

where $(CR)_0$ and $(CR)_1$ are the corrosion rates in the absence and presence of APT respectively.

2.4. Surface analytical techniques

SEM–EDX studies were carried out using JEOL JSM-6390LV/LGS Scanning Electron Microscope, USA and JEOL Model JED-2300, Energy Dispersive X-ray Analyzer, USA.

Table 6 Impedance parameters of Cu–Ni (90/10) alloy in seawater in the presence of 6.5 mM APT at different immersion periods. (Temperature: 30 °C).

Immersion period (h)	R_{ct} (k Ω cm 2)	C_{dl} (μ F cm $^{-2}$)	n_1	R_{film} (k Ω cm 2)	C_{film} (μ F cm $^{-2}$)	n_2	Error (%)	IE (%)
1	198.4	0.202	0.88	17.40	0.451	0.69	1.4	99.63
3	378.2	0.099	0.89	152.3	0.379	0.71	0.6	99.73
6	685.8	0.086	0.90	312.1	0.251	0.78	0.6	99.53
24	720.4	0.055	0.92	0.385	0.124	0.85	0.6	99.42
48	1713.0	0.032	0.95	572.3	0.110	0.89	0.7	99.72

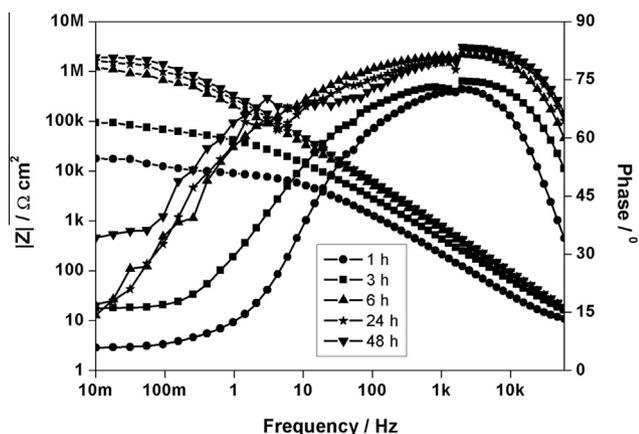
Table 7 Impedance parameters of Cu–Ni (90/10) alloy in seawater and Pre-filmed alloy in the presence of 6.5 mM APT in seawater at different temperatures. (Immersion period: 48 h).

Specimen	Environment	Temperature	R_{ct} ($k\Omega\text{ cm}^2$)	C_{dl} ($\mu\text{F cm}^{-2}$)	n_1	R_{film} ($k\Omega\text{ cm}^2$)	C_{film} ($\mu\text{F cm}^{-2}$)	n_2	Error (%)	IE (%)
Bare alloy	Seawater	30	4.72	12.20	0.67	0.02	15.12	0.66	0.7	–
Pre filmed alloy	Seawater + 6.5 mM APT	30	1713.0	0.032	0.95	572.3	0.110	0.89	0.7	99.72
Bare alloy	Seawater	40	2.972	8.38	0.71	0.004	72.52	0.57	0.6	–
Pre filmed alloy	Seawater + 6.5 mM APT	40	734.9	0.390	0.85	0.363	0.286	0.76	0.7	99.60
Bare alloy	Seawater	60	0.315	50.42	0.58	0.002	210.0	0.55	1.1	–
Pre filmed alloy	Seawater + 6.5 mM APT	60	389.0	0.706	0.81	184.9	0.616	0.76	0.6	99.91

3. Results and discussion

3.1. Electrochemical impedance studies

The Bode plots of Cu–Ni (90/10) alloy immersed in synthetic seawater for different immersion periods are shown in Fig. 1. The corresponding impedance parameters are given in Table 3. There is only one phase maximum in all these plots and the angle corresponding to the phase maximum is found to be in the range of 51–56°. The total impedance Bode plots indicate that impedance increases with immersion time. This result infers that with an increase in immersion time, the film becomes more and more protective. In these figures the $|Z|$ vs. f curves exhibit three different segments. In the high frequency region, the value of $|Z|$ tends to become very small and the corresponding phase angle also falls off very rapidly with increasing fre-

**Figure 6** Bode plots of Cu–Ni (90/10) alloy in synthetic seawater containing 10 ppm sulphide in the presence of 6.5 mM APT at different immersion periods. [Temperature: 30 °C].

quency. This region is typical of a resistive behaviour and corresponds to solution resistance. In the medium frequency region, a linear relationship exists between $|Z|$ and f and there is a broad maximum in phase angle vs. frequency plot. This region corresponds to the charge transfer at the metal/electrical double layer. In the low frequency segment, the resistive behaviour of the electrode increases and the value of $|Z|$ should remain constant with a further decrease in frequency. But such behaviour is not found. $|Z|$ still increases, with a decrease in frequency. This corresponds to the diffusion impedance because of diffusion of oxygen and chloride from bulk of the solution to the interface at the instant of immersion of the electrode in synthetic seawater and also diffusion of CuCl_2^- species from the interface into the bulk of the solution at higher immersion periods (Bacarella and Griess, 1973; Kear et al., 2004). In order to account for the above results, the metal/solution interface is modelled as per the equivalent circuit shown in Fig. 2A (Yuan and Pehkonen, 2007) and the best of the experimental results were obtained with this model. In this model constant phase element (CPE) is substituted for the double layer capacitance to give a more accurate fit (Bentiss et al., 1999). With an increase in immersion time from 1 to 48 h, the charge transfer resistance (R_{ct}) is found to increase from 0.722 to 4.720 $k\Omega\text{ cm}^2$. This result indicates that there is formation of a protective film of Cu_2O after 2 days immersion period.

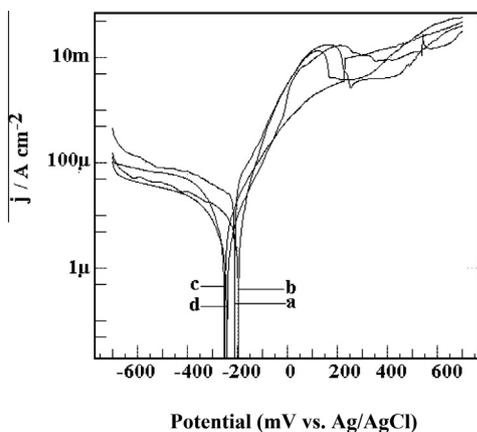
The Bode plots of Cu–Ni (90/10) alloy in seawater environment containing 10 ppm of sulphide ions at different immersion periods are shown in Fig. 3. These Bode plots show some interesting features. There is almost a merger of the plots for different immersion periods at higher frequencies. The phase angle Bode plots showed a clear shift in phase angle maximum towards lower frequencies with an increase in immersion period. However, the phase angle maximum is narrower in comparison to the corresponding plots in the absence of sulphide. The total impedance Bode plots show a linear behaviour in relatively less range of frequency in comparison

Table 8 Impedance parameters of Cu–Ni (90/10) alloy in seawater containing 10 ppm sulphide in the presence of 6.5 mM APT at different immersion periods. (Temperature: 30 °C).

Immersion period (h)	R_{ct} ($k\Omega\text{ cm}^2$)	C_{dl} ($\mu\text{F cm}^{-2}$)	n_1	R_{film} ($k\Omega\text{ cm}^2$)	C_{film} ($\mu\text{F cm}^{-2}$)	n_2	Error (%)	IE (%)
1	7.883	0.650	0.73	7.755	1.815	0.62	2.0	93.65
3	35.96	0.222	0.81	17.22	0.382	0.72	1.3	98.58
6	287.6	0.152	0.87	120.7	0.254	0.78	0.8	99.71
24	721.9	0.077	0.89	333.5	0.211	0.82	1.5	99.88
48	1011.0	0.065	0.90	571.6	0.197	0.86	0.7	99.90

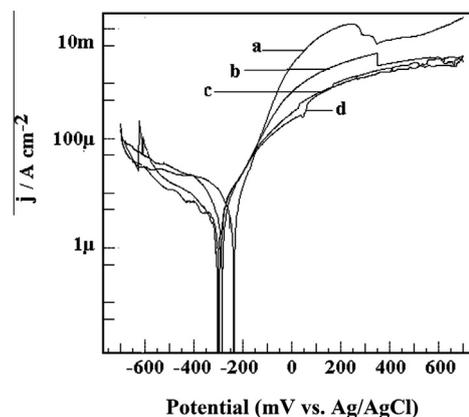
Table 9 Impedance parameters of Cu–Ni (90/10) alloy in seawater containing 10 ppm of inorganic sulphide and Pre-filmed alloy in the presence of 6.5 mM APT in seawater containing 10 ppm of inorganic sulphide at different temperatures. (Immersion period: 48 h).

Specimen	Environment	Temperature	R_{ct} ($k\Omega\text{ cm}^2$)	C_{dl} ($\mu\text{F cm}^{-2}$)	n_1	R_{film} ($k\Omega\text{ cm}^2$)	C_{film} ($\mu\text{F cm}^{-2}$)	n_2	Error (%)	IE (%)
Bare alloy	Seawater + 10 ppm sulphide	30	0.992	210.0	0.64	0.003	322.3	0.63	0.6	–
Pre filmed alloy	Seawater + 10 ppm sulphide 3.33 mM BTAH	30	1011.0	0.065	0.90	571.6	0.197	0.86	0.7	99.90
Bare alloy	Seawater + 10 ppm sulphide	40	0.390	168.8	0.58	0.002	434.6	0.57	0.6	–
Pre filmed alloy	Seawater + 10 ppm sulphide 3.33 mM BTAH	40	196.5	0.426	0.79	104.1	0.656	0.69	1.6	99.80
Bare alloy	Seawater + 10 ppm sulphide	60	0.184	256.1	0.54	0.002	525.6	0.54	1.2	–
Pre filmed alloy	Seawater + 10 ppm sulphide 3.33 mM BTAH	60	138.2	0.601	0.78	71.25	0.820	0.67	1.4	99.87

**Figure 7** Potentiodynamic polarization curves of Cu–Ni (90/10) alloy in synthetic seawater at different immersion periods. (a) 1 h, (b) 12 h, (c) 24 h, and (d) 48 h. [Temperature: 30 °C].

to the plots in the absence of sulphide ions. The total impedance is also found to be much less in comparison to the system containing no sulphides. The experimental data fitted well with the equivalent circuit shown in Fig. 2A. The impedance parameters are given in Table 4. Both the R_{ct} and film resistance (R_{film}) values are increased with an increase in immersion period. The C_{dl} and C_{film} are increased in the presence of sulphide ions. That means, by the addition of sulphide ions the protective nature of the film is reduced. However, both double layer and the film still show a combination of capacitive and resistive behaviours. Such a large increase in both C_{dl} and C_{film} in the presence of only 10 ppm S^{2-} ions shows the significant effect of S^{2-} in modifying especially the inner layer due to strong specific adsorption of sulphide (De Sanchez and Schiffrin, 1982; Sayed et al., 2003).

Fig. 4 shows the Bode plots of the Cu–Ni (90/10) alloy in seawater containing APT inhibitor at various concentrations and at a constant immersion period of 48 h. A close

**Figure 8** Potentiodynamic polarization curves of Cu–Ni (90/10) alloy in synthetic seawater containing 10 ppm sulphide at different immersion periods. (a) 1 h, (b) 12 h, (c) 24 h, and (d) 48 h. [Temperature: 30 °C].

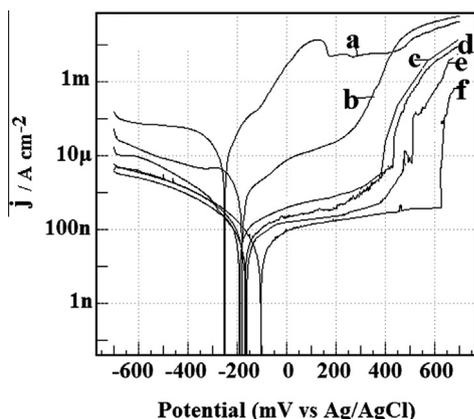
examination of Bode plots reveals interesting features. There is a possibility of two time constants. With an increase in concentration of the inhibitor to 6.5 mM, there is a shift in the phase maximum towards a higher frequency and phase angle is increased from 56 to 81°. The total impedance increased to a very great extent in the presence of the inhibitor. There is a large increase in total impedance and more broadening of the phase maximum with an increase in concentration of the inhibitor. This result reveals that the protective nature of the inhibitor film is increased with an increase in concentration of the inhibitor. The physical model may be thought of consisting of the metal/protective surface film/EDL/electrolyte solution. The experimental data fitted well with the equivalent circuit model shown in Fig. 2B and the impedance parameters are given in Table 5. It is interesting to note that both R_{ct} and R_{Film} are increased with an increase in concentration of the inhibitor. These results reveal that the concentration of APT molecules in the protective film is increased and the APT molecules replaced

Table 10 Corrosion parameters of Cu–Ni (90/10) alloy obtained by potentiodynamic polarization studies in seawater at different immersion periods. (Temperature: 30 °C).

Immersion period (h)	E_{corr} (mV)	i_{corr} ($\mu\text{A cm}^{-2}$)	β_c (mV dec ⁻¹)	β_a (mV dec ⁻¹)
1	–219.0	23.3	–165.0	86.8
12	–239.1	4.98	–105.0	90.8
24	–241.0	4.25	–78.1	84.8
48	–251.3	5.98	–115.0	68.2

Table 11 Corrosion parameters of Cu–Ni (90/10) obtained by potentiodynamic polarization studies in seawater containing 10 ppm of inorganic sulphide at different immersion periods. (Temperature: 30 °C).

Immersion period (h)	E_{corr} (mV)	i_{corr} ($\mu\text{A cm}^{-2}$)	β_c (mV dec^{-1})	β_a (mV dec^{-1})
1	-239.0	4.27	-138.0	78.0
12	-290.4	3.84	-130.4	81.6
24	-287.6	3.55	-122.0	65.9
48	-303.8	2.77	-191.0	93.4

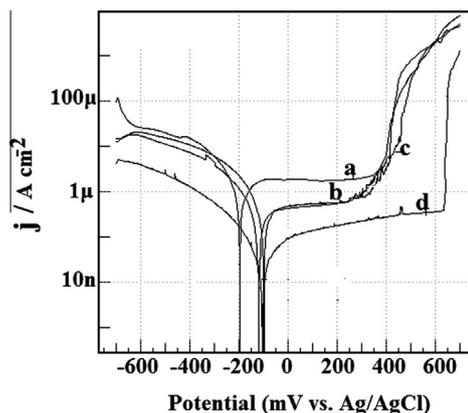
**Figure 9** Potentiodynamic polarization curves of Cu–Ni (90/10) alloy in synthetic seawater in the presence of different concentrations of APT at 48 h immersion period. (a) 0 mM, (b) 1.67 mM, (c) 2.50 mM, (d) 3.33 mM, (e) 5.0 mM, and (f) 6.5 mM. [Temperature: 30 °C].

almost all the water molecules and the ions in the electrical double layer. The corrosion inhibition efficiencies are calculated from the R_{ct} values in the absence and presence of APT using the Eq. (2).

$$\text{IE (\%)} = 100 \times \frac{[(R_{\text{ct}})^1 - (R_{\text{ct}})]}{(R_{\text{ct}})^1} \quad (2)$$

In equation, $(R_{\text{ct}})^1$ and (R_{ct}) are the charge transfer resistances in the presence and absence of APT respectively. An inhibition efficiency of 99.72% is obtained in the presence of 6.5 mM APT. Hence, 6.5 mM concentration APT is fixed for further studies.

The effect of immersion time in the range from 1 to 48 h on corrosion behaviour of Cu–Ni (90/10) alloy in synthetic seawater in the presence of 6.5 mM APT was studied. The corresponding Bode plots are shown in Fig. 5, which reveal some interesting features. Even after 1 h immersion period, there is enormous increase in phase maximum and total impedance

**Figure 10** Potentiodynamic polarization curves of Cu–Ni (90/10) alloy in synthetic seawater in the presence of 6.5 mM APT at different immersion periods. (a) 1 h, (b) 12 h, (c) 24 h, and (d) 48 h. [Temperature: 30 °C].

in comparison to the system in the absence of APT. With an increase in immersion period, there is a slight increase in phase maximum, while there is more broadening of phase maximum. The impedance parameters are given in Table 6. Both R_{ct} and R_{film} values are found to increase significantly with an increase in immersion period. The 'n' values corresponding to both CPE of double layer and of the film are found to increase with an increase in immersion period. These results reveal that the APT film becomes more protective with an increase in immersion period from 1 to 48 h.

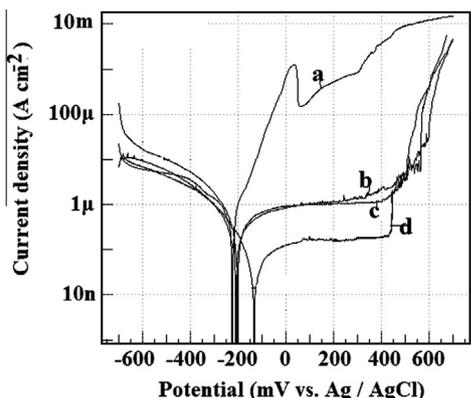
After the formation of the protective film on the Cu–Ni (90/10) alloy by immersing it in seawater containing 6.5 mM APT for 48 h, the effect of increase in temperature on the impedance behaviour of this pre-filmed alloy was studied in seawater containing 6.5 mM APT. The nature of Bode plots is similar to those plots at 30 °C (plots not shown). However, the total impedance and phase angle maximum values are reduced with an increase in temperature. Nevertheless, for the bare alloy also, the total impedance and phase angle maximum values

Table 12 Corrosion parameters of Cu–Ni (90/10) alloy obtained by potentiodynamic polarization studies in seawater in the presence of different concentrations of APT at 48 h immersion period. (Temperature: 30 °C).

Concentration of APT (ppm)	E_{corr} (mV)	i_{corr} ($\mu\text{A cm}^{-2}$)	β_c (mV dec^{-1})	β_a (mV dec^{-1})	IE (%)
0	-251.3	5.28	-115.0	68.2	—
1.66	-187.0	0.55	-69.8	62.2	89.58
2.50	-178.1	0.35	-67.2	0.60	93.37
3.33	-163.7	0.020	-66.1	56.7	99.62
5.0	-162.1	0.017	-52.3	52.0	99.68
6.5	-99.27	0.010	-32.0	41.2	99.81

Table 13 Corrosion parameters of Cu–Ni (90/10) alloy obtained by potentiodynamic polarization studies in seawater in the presence of 6.5 mM APT at different immersion periods. (Temperature: 30 °C).

Immersion period (h)	E_{corr} (mV)	i_{corr} ($\mu\text{A cm}^{-2}$)	β_c (mV dec $^{-1}$)	β_a (mV dec $^{-1}$)	IE (%)
1	-187.6	0.67	-110.0	152.0	97.12
12	-114.5	0.17	-96.7	147.0	96.59
24	-102.5	0.13	-60.7	84.7	96.94
48	99.27	0.01	-32.0	41.2	99.81

**Figure 11** Potentiodynamic polarization curves of Cu–Ni (90/10) alloy in synthetic seawater polluted with 10 ppm sulphide in the presence of 6.5 mM APT at different immersion periods. (a) 1 h, (b) 12 h, (c) 24 h, (d) 48 h [Temperature: 30 °C].

are reduced with an increase in temperature. The impedance parameters at three different temperatures for bare alloy and pre-filmed alloy after an immersion period of 48 h in seawater containing 6.5 mM APT are given in the Table 7. Both R_{ct} and R_{film} of the pre-filmed alloy are found to decrease with an increase in temperature. Nevertheless, these values are far higher than the corresponding values of the bare alloy. Hence, inhibition efficiencies >99% are obtained even at 40 and 60 °C. Both n_1 and n_2 values are decreased to some extent with an increase in temperature. All these results are indicative of the deviation of double layer and also of the film from more capacitive to less capacitive behaviour with an increase in temperature.

The results of the efficiency of APT in controlling corrosion of Cu–Ni (90/10) alloy in seawater containing sulphide ions are now discussed. In these studies, the concentration of APT is fixed at 6.5 mM. Fig. 6 shows the Bode plots of Cu–Ni (90/10) alloy in seawater environment containing 10 ppm of sulphide ions in the presence of 6.5 mM APT at different immersion periods. The Bode plots are broadened and the phase angle

maxima are increased at all immersion periods in comparison to those in the absence of APT. The phase angle maximum is shifted towards a much higher frequency region. At 6, 24 and 48 h immersion periods, the total impedance plots show linearity from the highest frequency of 60 kHz to the lowest frequency of 10 mHz. The experimental results fitted well with the same equivalent circuit shown in Fig. 2B and the impedance parameters are given in Table 8. Both R_{ct} and R_{film} values are found to increase enormously in the presence of the inhibitor and also with an increase in immersion period. After 48 h immersion period, the R_{ct} and R_{film} values respectively are 1011 and 571.6 k Ω cm 2 . The C_{dl} is reduced from 93.02 $\mu\text{F cm}^{-2}$ to an extremely small value of 0.650 $\mu\text{F cm}^{-2}$ in the presence of APT even at 1 h immersion period. This result indicates the absence of all corrosive ions present in seawater and sulphide ions and presence of only APT molecules in the double layer. The n values are found in between 0.73 and 0.90.

Once again after the formation of protective film on the alloy by immersing it in seawater containing 10 ppm sulphide and 6.5 mM APT, the effect of increase of temperature on the impedance behaviour of this pre-filmed alloy has been studied. This can be understood from the impedance parameters given in Table 9. Both R_{ct} and R_{film} are reduced with an increase in temperature. Both n_1 and n_2 are reduced to some extent. Nevertheless, the inhibition efficiencies are greater than 99% in the entire temperature range. Thus, impedance studies reveal that APT functions well in the entire temperature range studied.

3.2. Potentiodynamic polarization studies

The potentiodynamic polarization curves for Cu–Ni (90/10) alloy in synthetic seawater in the potential range from -0.7 to +0.7 V vs. Ag/AgCl/1.0 M KCl are shown in Fig. 7 and the corrosion parameters are given in Table 10. The anodic polarization curves show three distinct regions namely Tafel region at lower over potentials extending to the peak current density due to dissolution of copper to Cu^+ ions, a region of decreasing current density until a minimum (i_{min}) is reached due to formation of CuCl and a region of sudden increase in current density leading to a limiting value (i_{lim}), due to formation of

Table 14 Corrosion parameters of Cu–Ni (90/10) alloy obtained by potentiodynamic polarization studies in seawater containing 10 ppm sulphide in the presence of 6.5 mM APT at different immersion periods. (Temperature: 30 °C).

Immersion period (h)	E_{corr} (mV)	i_{corr} ($\mu\text{A cm}^{-2}$)	β_c (mV dec $^{-1}$)	β_a (mV dec $^{-1}$)	IE (%)
1	-234.1	0.54	-149.0	103.0	87.35
12	-203.3	0.13	-99.8	98.8	96.62
24	-201.3	0.09	-48.3	54.4	97.46
48	-131.4	0.02	-56.1	74.1	99.28

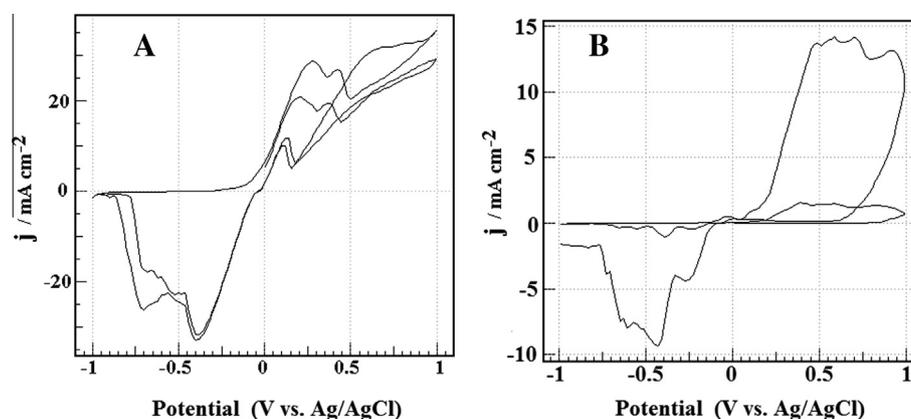


Figure 12 Cyclic voltammograms of Cu–Ni (90/10) alloy in synthetic seawater in the (A) absence and (B) presence of 6.5 mM APT after 48 h immersion period. [Temperature: 30 °C].

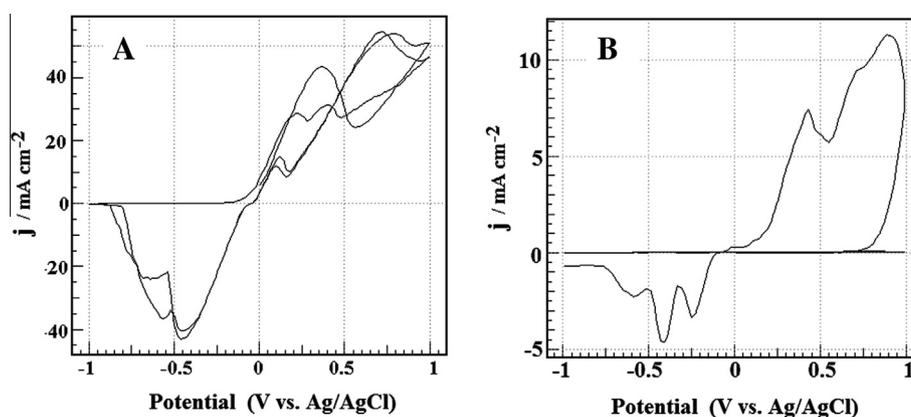


Figure 13 Cyclic voltammograms of Cu–Ni (90/10) alloy in synthetic seawater polluted with 10 ppm sulphide in the (A) absence and (B) presence of 6.5 mM APT after 48 h immersion period. [Temperature: 30 °C].

CuCl_2^- . These three regions have been reported in the literature in the polarization curves of copper in 3.5% sodium chloride solution (Kear et al., 2004) and also in the case of Cu–Ni (90/10) alloy (Babic et al., 1999). With an increase in immersion period from 1 to 48 h, the corrosion potential (E_{corr}) is shifted towards a more negative value. However, the corrosion current density (i_{corr}) is found to decrease significantly up to 12 h immersion period and then increase slightly up to 48 h. These results summarize that with an increase in immersion period from 1 to 48 h, there is a decrease in the corrosion rate of the alloy due to the formation of copper oxide film, and this has been extensively reported by many investigators (Kato et al., 1980; Wang et al., 1994; Druska et al., 1996; Popplewell et al., 1973). Another interesting feature is that while there is only one anodic peak after 1 and 12 h immersion periods, there are two anodic peaks after 24 and 48 h immersion periods at +150 and +250 mV electrode respectively. The larger peak at +150 mV is due to oxidation of Cu to Cu^+ ions and the smaller peak at +250 mV is due to oxidation of Cu^+ to Cu^{2+} ions.

The potentiodynamic polarization curves of Cu–Ni (90/10) alloy in seawater containing 10 ppm sulphide are depicted in Fig. 8. The corrosion potential is shifted towards more negative potentials by the addition of 10 ppm sulphide. The

corrosion parameters are given in Table 11. With an increase in immersion time, the shift in β_c is much higher than the shift in β_a . This is due to depletion of sulphide with an increase in immersion time as a consequence of the formation of a thick cuprous sulphide film at the surface (Macdonald et al., 1979). The main effect of copper sulphide is to accelerate the charge transfer of oxygen reduction, thereby controlling the reduction current density by a diffusive transport through the liquid layer adjacent to the electrode and this is manifested as an increase in β_c (De Sanchezis and Schiffrin, 1982; Kato et al., 1984).

The potentiodynamic polarization curves of Cu–Ni (90/10) alloy in seawater in the presence of different concentrations of APT are shown in Fig. 9. The corrosion parameters are given in Table 12. The E_{corr} is shifted towards less negative potentials in comparisons to absence of APT. The E_{corr} is also shifted towards less negative potentials with an increase in concentration of APT. The corrosion current density significantly decreases with the addition of 1.67 mM APT and it decreases further with increase in concentration of the inhibitor to 6.5 mM. Another significant effect is on anodic peak potential and peak current in the presence of the inhibitor. The two characteristic anodic peaks appeared in the polarization curve in seawater without inhibitor are practically absent in the presence of

Table 15 Weight-loss data of Cu–Ni (90/10) alloy in seawater and 10 ppm of inorganic sulphide containing seawater in the absence and presence of different concentrations of APT after 30 days immersion period. (Temperature: 30 °C).

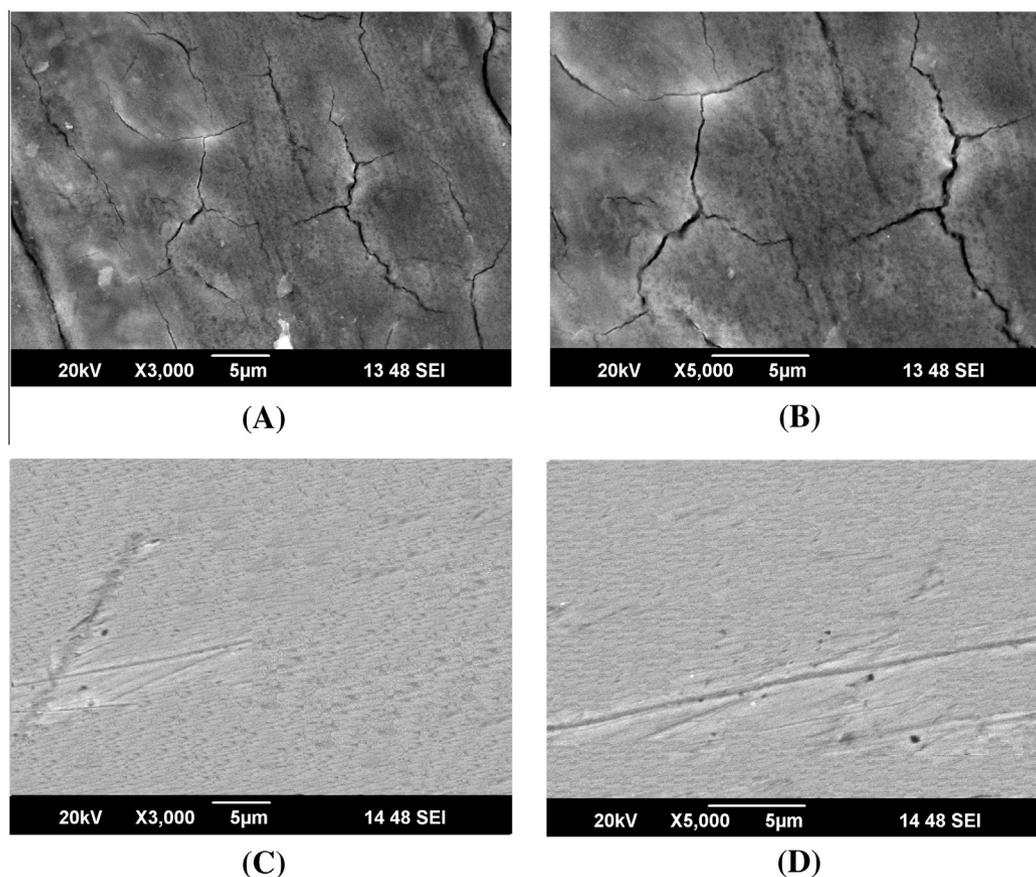
Environment	Weight before immersion (W_1) (g)	Weight after immersion (W_2) (g)	Weight loss (ΔW) (g)	Corrosion rate (mmpy)	IE (%)
Seawater	8.10845	8.09889	0.00956	0.01295	–
Seawater + 10 ppm sulphide	8.26840	8.25173	0.01667	0.02258	–
Seawater + 5.0 mM APT	8.14125	8.14039	0.00086	0.00117	91.00
Seawater + 6.5 mM APT	7.72131	7.72127	0.00004	0.00005	99.58
Seawater + 10 ppm sulphide + 5.0 mM APT	8.15593	8.15498	0.00095	0.00129	90.02
Seawater + 10 ppm sulphide + 6.5 mM APT	5.56154	8.56150	0.00004	0.00005	99.76

inhibitor. The current values in the entire anodic region are greatly reduced in the presence of the inhibitor. Another interesting feature is to be noted in the anodic polarization curve at 6.5 mM concentration of the inhibitor. The entire anodic region up to +600 mV vs. Ag/AgCl has become passive with extremely low current of $< 1 \mu\text{A cm}^{-2}$ (against mA cm^{-2} in the absence of inhibitor). It may be noted that the passivity breaks down at +600 mV. The anodic Tafel slope and cathodic Tafel are shifted in the presence of APT. Hence, it is inferred that APT acts as a mixed inhibitor. The inhibition efficiencies were calculated using the equation 3.

$$\text{IE (\%)} = 100 \times \frac{[(i_{\text{corr}}) - (i_{\text{corr}})^1]}{(i_{\text{corr}})} \quad (3)$$

In the Eq. (3), (i_{corr}) and $(i_{\text{corr}})^1$ are the corrosion current densities of Cu–Ni (90/10) alloy in synthetic seawater in the absence and presence of APT respectively. The inhibition efficiency is found to be in the range of 89.58–99.81% within the concentration range studied.

The potentiodynamic polarization curves of the alloy in seawater in the presence of 6.5 mM APT at different immersion periods are depicted in Fig. 10. The corrosion parameters are given in Table 13. The E_{corr} is shifted to less negative potentials with an increase in immersion period. It is interesting to note that the protective nature of the film is evidenced even at 1 h immersion period itself by a large reduction in corrosion current density from 23.3 to $0.67 \mu\text{A cm}^{-2}$ and a passive

**Figure 14** SEM images of Cu–Ni (90/10) alloy in synthetic seawater in the absence (A-3000×, B-5000×) and presence (C-3000×, D-5000×) of 6.5 mM APT for a period of 30 days.

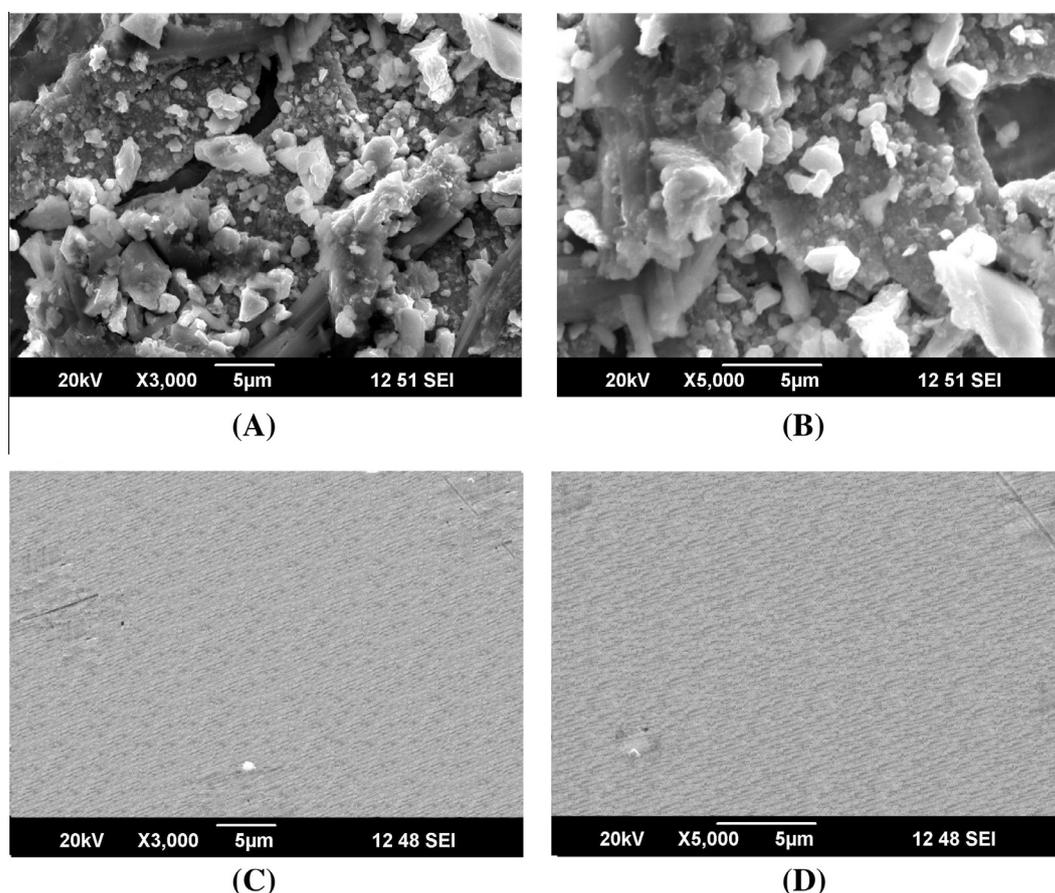


Figure 15 SEM images of Cu–Ni (90/10) alloy in synthetic seawater containing 10 ppm sulphide in the absence (A-3000 \times , B-5000 \times) and presence (C-3000 \times , D-5000 \times) of 6.5 mM APT for a period of 30 days.

anodic region up to +400 mV. However, with increase in immersion period up to 48 h, the i_{corr} is further reduced to $0.01 \mu\text{A cm}^{-2}$ and the passive anodic region is extended up to +600 mV.

When 6.5 mM of APT is added to the environment containing seawater and 10 ppm S^{2-} , the corresponding polarization curves of the alloy at different immersion periods show some interesting features (Fig. 11). The corrosion parameters obtained from these studies are given in Table 14. After 1 h immersion period, the same three regions, which are seen in the absence of APT, are found. But, reduction of corrosion current density is observed. After 48 h immersion period, the i_{corr} is further reduced to $0.01 \mu\text{A cm}^{-2}$ and the passive anodic region is found up to +450 mV. Regarding E_{corr} , it is shifted towards less negative potentials in the presence of inhibitor at all immersion periods in comparison to the control solution. The potentiodynamic polarization studies infer that the APT acts as a mixed inhibitor.

3.3. Cyclic voltammetric studies

The cyclic voltammograms of Cu–Ni (90/10) alloy after an immersion period of 48 h in seawater and seawater containing APT in the potential range from $-1.0 + 1.0 \text{ V vs. Ag/AgCl}$ are given in Figs. 12A and B respectively. In the first cycle, in the forward sweep, two anodic peaks are observed. The first

peak at +250 mV is due to $\text{Cu}-\text{Cu}^+$ couple and the second one at +450 mV is due to $\text{Cu}^+-\text{Cu}^{2+}$ couple. Two corresponding reduction peaks are observed in the reverse sweep (Wilhelm et al., 1982; Strehblow and Titze, 1980; Aruchamy and Fujishima, 1989). In the second cycle, a similar behaviour is seen. Both anodic and cathodic peak currents are increased to some extent in the second cycle. In the presence of 6.5 mM APT, in the first cycle there is no anodic peak up to +850 mV. In the second cycle, similar behaviour of bare alloy in the absence of APT is observed. This is due to the breakdown of the protective APT film, when polarized to a higher anodic potential such as +1.0 V. The CV profiles confirm that APT inhibitor functions excellently and protects the Cu–Ni (90/10) alloy from corrosion in a seawater environment. Similar performance of APT inhibitor is also exhibited in the in seawater containing 10 ppm sulphide ions as depicted in Fig. 13.

3.4. Gravimetric studies

The results of gravimetric studies of Cu–Ni (90/10) alloy in seawater and 10 ppm seawater containing sulphide in the absence and presence of two different concentrations of APT after an immersion period of 30 days are shown in Table 15. The concentrations of APT are chosen based on the inhibition efficiencies obtained from electrochemical studies. Essentially these studies are carried out to find out the efficiency of the

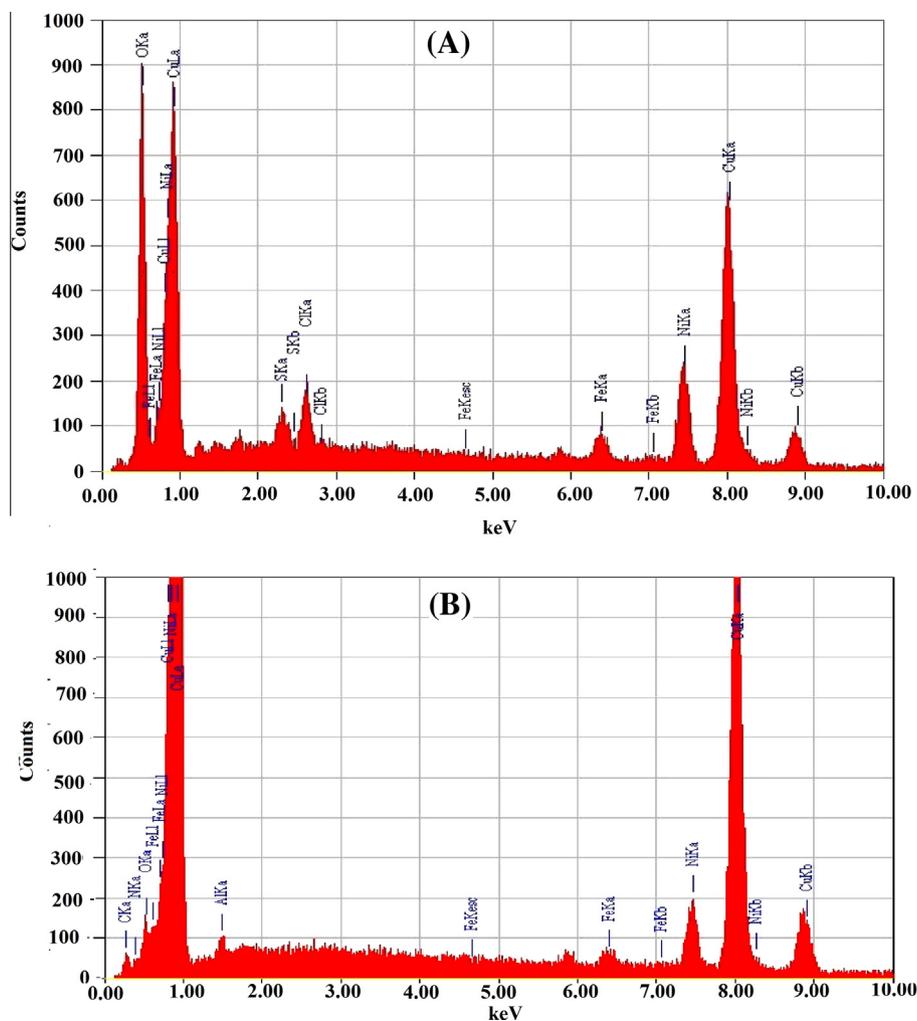


Figure 16 EDX spectra of Cu–Ni (90/10) alloy in synthetic seawater in the (A) absence and (B) presence of 6.5 mM APT for a period of 30 days.

inhibitor after a long immersion period, such as 30 days. When 5.0 mM APT is added to seawater and seawater containing sulphide, the corrosion rates are decreased significantly. However, when the concentration of APT is increased to 6.5 mM, negligible weight-loss is observed in both environments, accounting for inhibition efficiency greater than 99%. Thus, the results of gravimetric studies revealed that the APT proved to be an excellent inhibitor even after an immersion period of 30 days.

3.5. Scanning electron microscopy (SEM)/energy dispersive X-ray analysis (EDX)

Scanning electron micrographs of Cu–Ni (90/10) alloy in seawater in the absence of APT after 30 days immersion at two different magnifications are shown in Figs. 14A and B respectively. These micrographs clearly show that the surface is severely corroded and there is formation of different forms of corrosion products on the alloy surface. Breakdown of oxide film is also seen. The SEM images of the alloy in seawater

containing 10 ppm sulphide are shown in Figs. 15A and B, which show that the corrosion damage of the alloy is more severe. The entire surface is covered by a scale like black corrosion product and severe pits are also seen. But, in the presence of APT in seawater (Fig. 14C and D) as well as sulphide containing seawater (Fig. 15C and D), the surface is completely smooth and there is absence of any corrosion. These micrographs reveal the image of the protective APT film.

The EDX spectrum in the absence of APT in seawater (Fig. 16A) infers the presence of large amount of Cu_2O as indicated by the very high intensity of O signal. In seawater containing sulphide (Figs. 17A), the EDX spectrum shows a signal due to S in addition to the O signal. These results reveal that the corrosion products contain both Cu_2O and Cu_2S in seawater containing 10 ppm sulphide. However, in the presence of APT in seawater (Fig. 16B) and seawater containing sulphide (Fig. 17B), the EDX spectra show only those signals, which are characteristic of the existence of C and N present in the APT molecule. The intensity of O signal is significantly reduced and the signal due to S is completely absent.

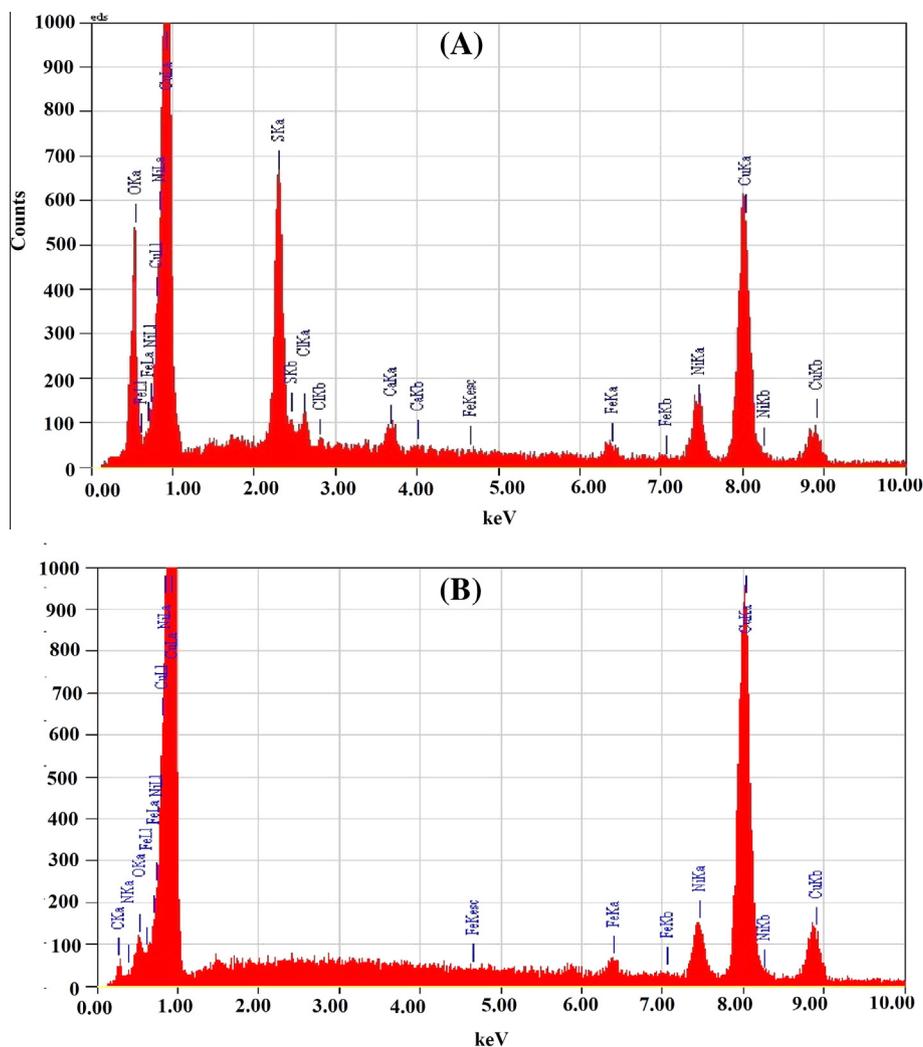


Figure 17 EDX spectra of Cu–Ni (90/10) alloy in synthetic seawater containing 10 ppm sulphide in the (A) absence and (B) presence of 6.5 mM APT for a period of 30 days.

Table 16 Comparison of inhibition efficiency of 5-(3-aminophenyl)tetrazole for Cu–Ni (90/10) alloy with other heterocyclic organic compounds reported in the literature.

Compound	Environment	IE (%)	References
5-(3-Aminophenyl)tetrazole	Seawater	99.9	Present study
Histidine	0.25 M Na ₂ SO ₄	90.0	Badawy et al. (2005)
Phytic acid	3.4% NaCl	90.6	Hao et al. (2008)
Bis(diethyldithiocarbamate)	3.4% NaCl	79.0	Metikoš-Huković et al. (2011)
1,2,3-Benzotriazole	Seawater	99.9	Appa Rao et al. (2012)
1,2,3-Benzotriazole	0.5 M H ₂ SO ₄	98.0	Maciel et al. (2008)

3.6. Comparison of inhibition efficiency of 5-(3-aminophenyl)tetrazole with other heterocyclic organic compounds

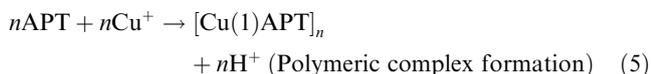
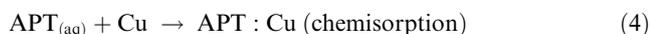
A comparison of inhibition efficiency of 5-(3-aminophenyl)tetrazole for Cu–Ni (90/10) alloy with other heterocyclic organic compounds in different corrosive environments reported in the literature is given in Table 16. APT exhibits 99.9% of inhibition efficiency (IE %) even in higher aggressive environment

i.e., seawater. This IE % is higher than the efficiencies of some of the heterocyclic organic compounds in relatively lower aggressive environments than seawater. Its inhibition efficiency is comparable to that of 1,2,3-benzotriazole.

3.7. Mechanism of corrosion inhibition by APT

The mechanisms of corrosion of Cu–Ni (90/10) alloy in seawater and sulphide-containing seawater have been reported in the

literature (Walton and Brrok, 1977; De Sanchezis and Schiffrin, 1982; Al-Hajji and Reda, 1995; Allam et al., 2005). When the inhibitor, APT is added to seawater and seawater containing sulphide, chemisorption of APT on the alloy surface occurs first, followed by the formation of a polymeric complex, as shown in Eqs. (4) and (5).



The polymeric complex, $[\text{Cu(I)APT}]_n$ forms a protective film and inhibits corrosion of the alloy in seawater and seawater containing sulphide.

4. Conclusions

1. All the studies employed in the present study reveal that 5-(3-aminophenyl)tetrazole (APT) is proved to be an excellent inhibitor for Cu–Ni (90/10) alloy in synthetic seawater and synthetic seawater containing sulphide ions.
2. Electrochemical impedance studies show an enormous increase in both charge transfer resistance and the film resistance of the Cu–Ni (90/10) alloy in the presence of APT inhibitor. The protective APT film withstands even up to 60 °C.
3. Potentiodynamic polarization studies provide valuable information regarding the anodic behaviour of Cu–Ni (90/10) alloy in the absence and presence of APT, which is proved to function as a mixed inhibitor, predominantly anodic in nature.
4. Cyclic voltammetric studies show the stability of the protective film even at anodic potentials of 850 mV vs. Ag/AgCl.
5. APT is proved to be an excellent inhibitor even after an immersion period of 30 days, as evidenced by gravimetric studies
6. Surface examination studies by SEM–EDX, confirm the presence of protective APT film and absence of any corrosion products on the alloy surface.

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