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COPPER-AZOLE INHIBITIVE COMPLEXES IN CHLORIDE MEDIA-I

R RAVI, G RAJAGOPAL, R SRINIVASAN, N PALANISWAMY and K BALAKRISHNAN
Central Electrochemical Reserach Institure, Karaikudi-632006

ABSTRACT

Copper-azole complexes were formed on copper elecrode surfaces immersed in media (pH 5 and 7) containing benzotriazole (BTA) and 2-mercaptobenzothiazole (MBT) with admixture of chloride, when the potential of the electrode was stepped up from -0.5V (SCE) to +0.2 V. The growth of the surface layers was monitored by observing changes in the reflectance of the electrode surface at different wavelengths in the visible spectrum. It was observed that the nature of the surface layers was determined by the concentration of the inhibitor present. The surface layers formed at concentrations of 2 ppm or more showed a characteristically higher reflection (lower values of Δ R/R%) in the green region, than at other wavelengths. Further, the level of change in CRP (approx. 60% for MBT and 10% for BTA) at the end of 4 minutes at pH 7 indicates that MBT is less protective than BTA. It is also seen that at higher concentrations, BTA is less protective at pH 5 (CRP approx. 30%) than at pH 7 (CRP approx. 10%) indicating the effectiveness of BTA as an inhibitor at pH 7. The phase angle was also measured, for some of the films formed at different inhibitor concentrations on an ellipsometer.

Key Words: Inhibitor, Phase angle measurement, Reflectance measurement

INTRODUCTION

The corrosion inhibition of copper surfaces immersed in media containing an azole type inhibitor has been shown [1-3] to be due to the formation of Cu-inhibitor complexes through bonding between the surface copper atoms and the N-atom on the inhibitor molecules. It has been found [4] that the formation of the complex on a surface already covered with a layer of Cu_2O is easier. These complexes act as a barrier and inhibit both anodic and cathodic reactions [5]

All the above results were obtained from electrochemical experiments or from ex-situ techniques such as Auger Electron Spectroscopy. In the present paper we report the study of surface layer formation by an in-situ technique in which change in reflectance of a copper surface anodically polarised at +0.2V vs SCE in media containing admixtures of inhibitor and chloride ions is monitored.

EXPERIMENTAL

Experimental details have been already described [6]. In the present experiments, the inhibitors used were 2-meraptobenzothiazole (0-5 ppm) and benzotraizole (0-30 ppm). The concentration of chloride in the media varied from 0 to 300 ppm. The reflection from the electrode surface was monitored for 4 mins. after the potential was stepped up from -0.5 to +0.2 V. The phase change P for polarized light at 546 nm reflected by the electrode surface was measured on an ellipsometer at the end of some of the experimental runs.

RESULTS AND DISCUSSIONS

The variation of Δ R/R% (CRP = Change in reflection percent) [6] with time for various media at pH 5 and 7 have been shown Figs.1 and 2 for mercaptobenzothiazole and in Figs.3 and 4 for 1:2:3 benzotriazole.

At pH 7 in the pure chloride media the reflection in red region is higher than at other wave lengths as can be expected from the presence of cuprous oxide.

With the addition of inhibitor (lower concentration) the reflection is higher in violet region in the case of BTA and in the green region in the case of MBT.

At pH 5 in the absence of the inhibitors, it is observed that the reflections in the violet and green regions are almost the same whereas it is slightly less for red.

With the addition of lower concentration of inhibitor, the reflection in the green region increases in the case of BTA.

In the pure chloride medium, it has been reportd [7] that the electrode surfaces were observed to be red or red-brown in colour with the inclusions of large purple areas at the end of the experiments. The layers formed on the surfaces were lonsely adherent suggesting a large degree of structural disorder. The layers were not uniformly formed over the whole surface but had a number of spots where the bright meta. showed through. It can be concluded that the film formed at the lower concentration of inhibitor and in pure chloride media includes chloride to a limited extent and is essentially a Cu_2O layer. The passivation of copper with the formation of CuCl complex has also been reported [8] by many workers. The results of the present work agree with these observations in that the higher reflection in red or violet is observed and visual examination of the electrode surface also showed the presence of large areas with these colours.

At higher inhibitor concentrations at pH 5 it was observed that the reflection in green region increases for both the inhibitors. For pH 7 it was observed that the reflection for violet is higher than the other two wavelengths for BTA whereas the reflection was higher in the green region for MBT. The visual observations showed that the films formed were very thin and the surface retained its brightness at the end of the experiment. There is a difference between surface immersed at higher concentrations

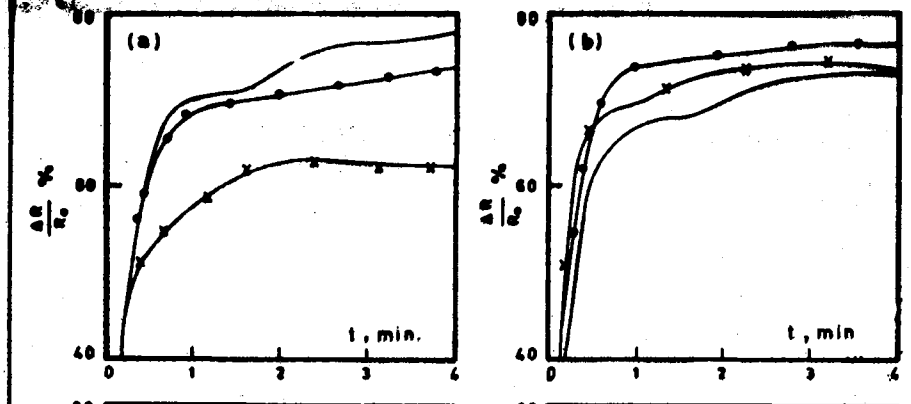

Fig. 1. Variation of Δ R/R% with time for various Concentrations of Chloride and MBT at pH 5 and at Different Wavelengths
a) 300 ppm Cl^- + 0.5 ppm MBT
b) 300 ppm Cl^- + 1.25 ppm MBT
c) 300 ppm Cl^- + 2.5 ppm MBT
d) 300 ppm Cl^- + 5 ppm MBT
— Red -o- Green -x- Violet

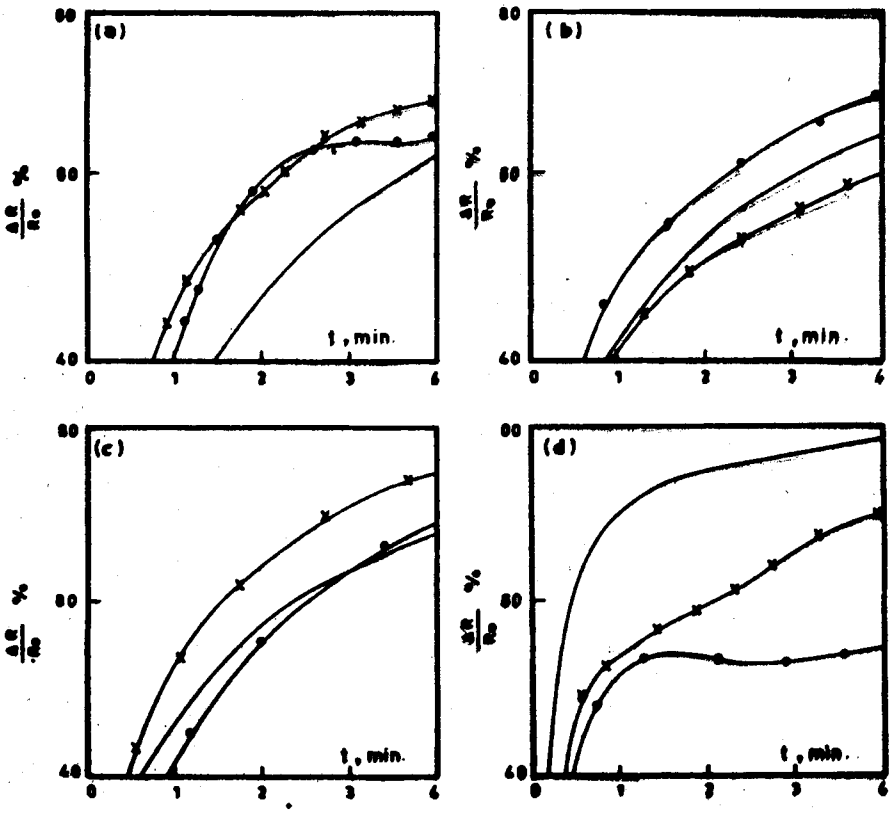

Fig.2. Variation of ΔR/R% with time for various Concentrations of Chloride and MBT at neutral pH 5 and at Different Wavelengths
a) 300 ppm Cl^- alone
b) 300 ppm Cl^- + 0.5 ppm MBT.
c) 300 ppm Cl^- + 1.25 ppm MBT.
d) 300 ppm Cl^- + 5 ppm of MBT
— Red -o- Green -x- Violet

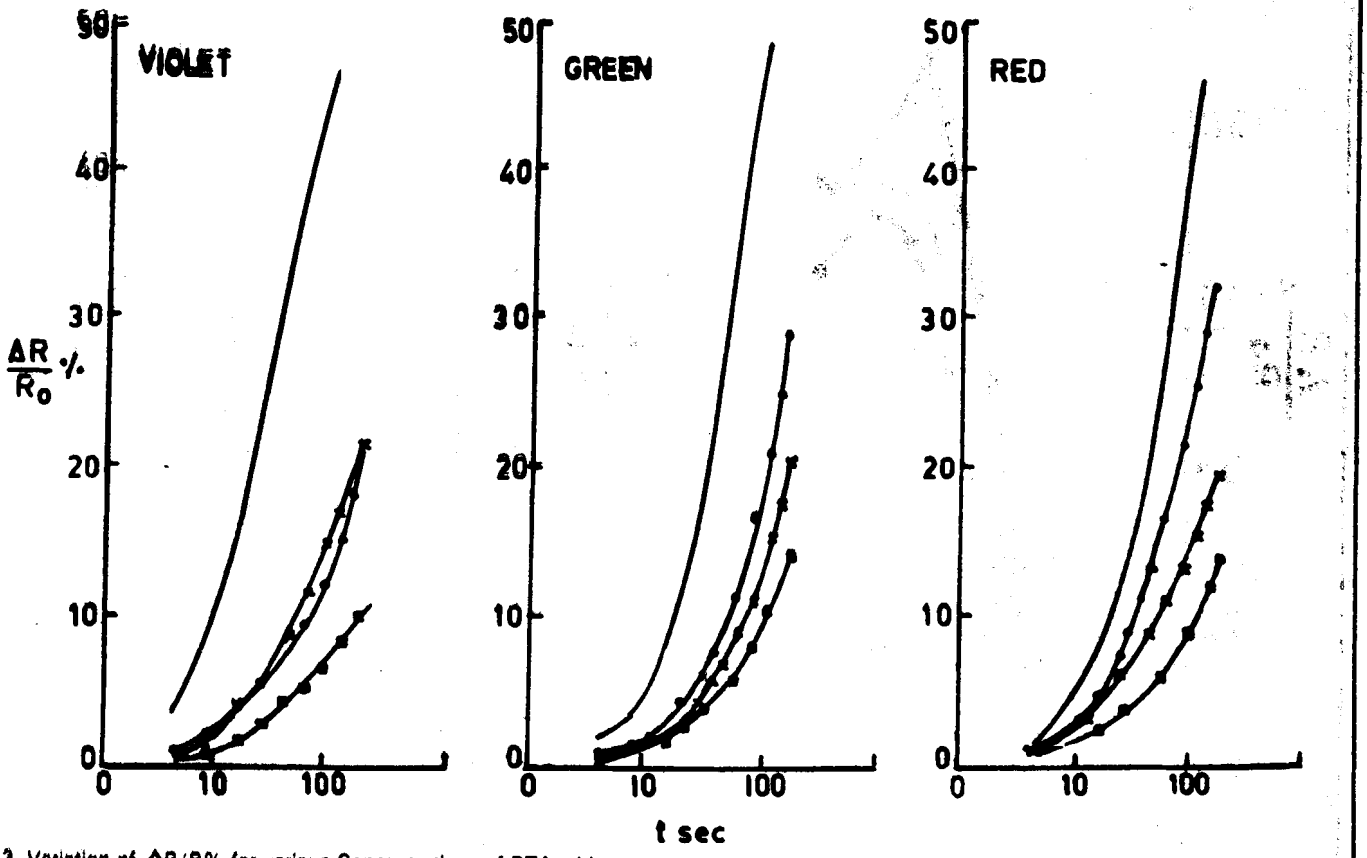

Fig. 3. Variation of ΔR/R% for various Concentrations of BTA with time at Neutral pH

—300 Cl^- —●— 300 Cl^- + 10 ppm BTA

—×— 300 ppm Cl^- + 15 ppm BTA

—— 300 ppm Cl^- + 20 ppm BTA

in BTA and that in MBT as indicated by the level of change in CRP (approx. 10% for BTA and approx. 60% for MBT). Thus at the higher concentrations of inhibitors, there is likely to be a thin non-uniform surface film of Cu^{2+} ions (as indicated by higher reflection in the green region [9] or the incorporation of inhibitive molecules in the surface layer.

It has been reported [10] that there is a critical minimum concentration above which the inhibitive effects are manifested. In our case this can be inferred from the drastic change in the reflection characteristics (increased reflection in green and violet for BTA and in green for MBT) as the inhibitor concentration is increased. (Fig 2 and Fig 3)

At pH 5 it is observed that the slope of the curve tends to zero after about 2 minutes indicating that the film formation process in this case is completed within the timespan of the experiment. On the other hand at pH 7 the change in reflection continues to increase. The CRP changes for pH 5 are higher than for pH 7 suggesting the less protective nature of the inhibition at lower pH values.

Table I shows the variation at pH 7 of the phase angle P, measured on an ellipsometer, for various concentrations of MBT and at various wavelenghts of incident light.

Table I: Variation of phase angle P at pH 7 for MBT with concentration and incident wavelength

Concn. of MBT (ppm)	White light	Wavelength of incident light		
		670 nm	550 nm	425 nm
0	22.0°	21.5°	19.0°	20.2°
0.5	23.5°	23.5°	18.0°	18.5°
1.25	24.0°	24.0°	20.0°	17.4°
2.5	10.0°	13.4°	15.0°	13.7°
5.0	16.4°	37.0°	33.0°	24.5°

It can be seen from Table-I that the nature of the film changes for concentrations greater than 1.25 ppm. The P values are similar for lower concentrations and up to 1.25 ppm indicating similar values for the surface layer thickness (P is related to thickness). The composition of this film is likely to be cuprous oxide/chloride. At 2.5 ppm the P values show a sudden decrease and then increase at higher concentration. Thus, at 2.5 ppm a thinner film is formed but this film is more protective (as indicated by

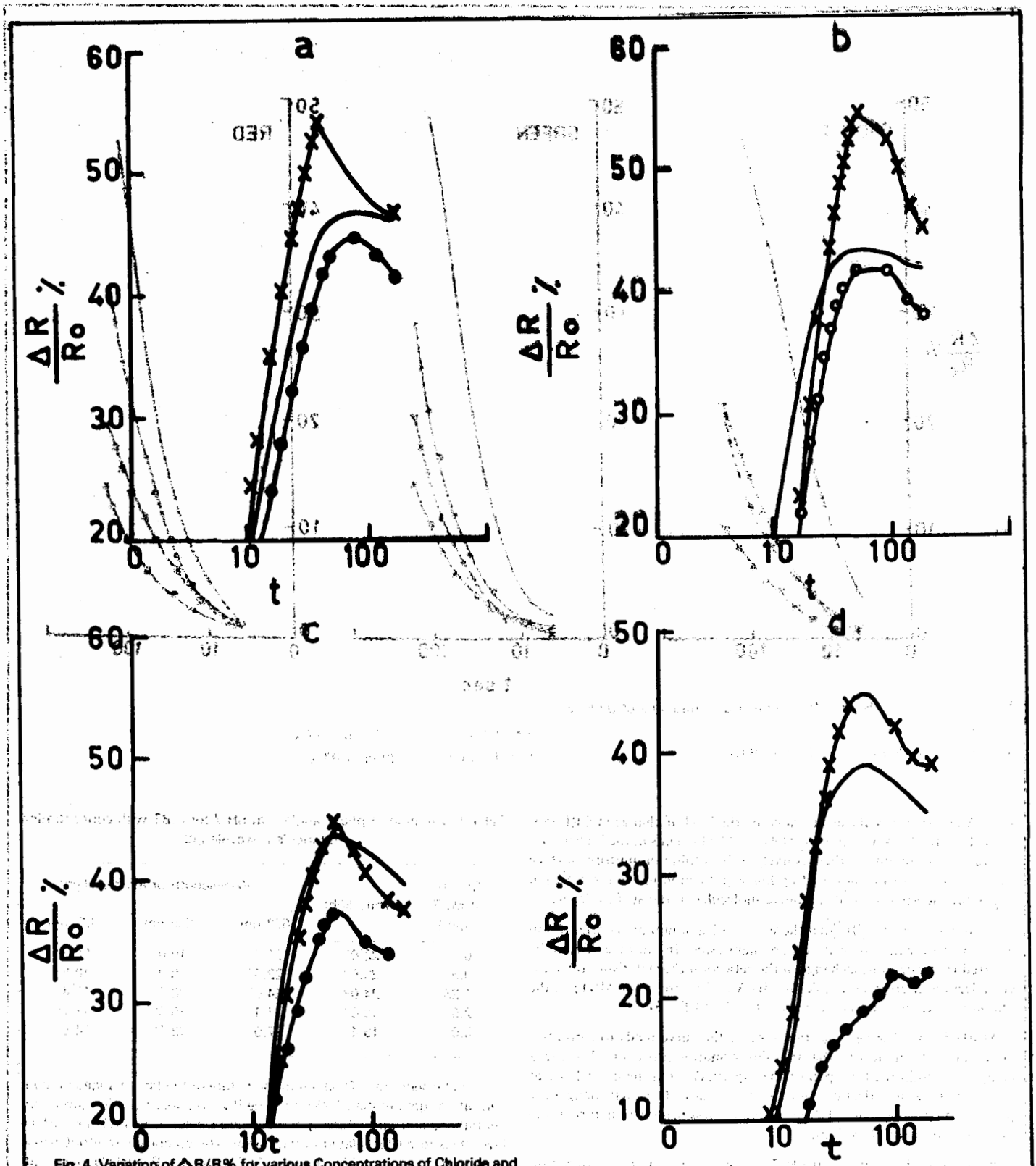

Fig. 4. Variation of ΔR/R% for various Concentrations of Chloride and BTA at pH 5 and at Different Wavelengths

a) 300 ppm Cl^-

b) 300 ppm Cl^- +1 ppm of BTA

c) 300 ppm of Cl^- + 2 ppm of BTA

d) 300 ppm of Cl^- + 5 ppm OF BTA

—×— Red —●— Green —— Violet

visual observations and changes in CRP). The thickness of this more protective film increases as the concentration subsequently rises to 5 ppm.

It can be futher seen that the growth of this film is dependent on the wavelength of light incident on the electrode surface. When the light of lower wavelengths are incident on the electrode surface, the film growth is seen to be curtailed as seen from the smaller changes in P for violet region. An earlier study[11]shows that the oxide growth on copper surface is essentially dependent on the radiation incident on the electrode surface and this has been attributed to the photoconductive nature of the oxide. It would be of interest to examine this aspect further from the point of view of ascertaining the photoconductive nature of the complexes as well.

CONCLUSION

MBT is less effective than BTA as can be seen from changes in CRP (approx. 60% for MBT and 10% for BTA). BTA is more effective at higher concentrations at pH 7 than at pH 5 though film formation at pH 5 is completed in less time than at pH 7. The film formed at pH 5 is apparently less protective as indicated by larger CRP values (approx. 30% at pH 5). The nature of the film formed is dependent on the pH as indicated by the reflection characteristics and also on the inhibitor concentration (as indicated by the change in CRP). Above a certain concentration the reflections in the green and violet regions (for BTA at neutral pH) are higher than those at the other wavelengths and the metallic lustre of the surface is not affected. This indicates that there is a critical minimum concentration for the inhibitor to be effective.

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