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Study on the synergistic effects of additives on the copper corrosion inhibitors

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Abstract : The influence of Sodium Benzoate (SB), Potassium Iodide (KI) and Thiourea (TU), on the inhibitive effect of Benzotriazole (BT) and Tolyltriazole (TT) in acidic medium (pH3) was investigated and Electrochemical Impedance Spectroscopy (EIS), Potentiodynamic Polarization and Open Circuit Potential (OCP) methods were used. Results showed that the inhibitive effect of BT and TT increased synergically in the presence of these additives. From the values of R_{ct}, C_{dl} and R_p, it was found that the synergistic effect of additives follow the order KI>SB>TU in their optimum concentration. Upon addition of these additives, a synergistic effect on inhibition performance of BT and TT was observed as indicated by impedance and polarization transient curves; also it was found that the OCP shifted towards more positive potentials after adding these chemicals. The strong adsorption of Benzotriazole and Tolyltriazole on the metal surface, which also contributes on the corrosion inhibition of substrate have been concluded.

Keywords : Corrosion inhibitor; Benzotriazole; Tolyltriazole; Synergistic effect; Electrochemical method.

INTRODUCTION

Application of Corrosion Inhibitors is among the most important methods in protecting metal surfaces from corrosion. The inhibition properties of Benzotriazole on copper was first introduced in 1947 and since then this chemical and its derivatives have been used widely as copper and copper alloys corrosion inhibitors and anti tarnish agents[1]. Further more Benzotriazole anti corrosion properties has also been investigated on other metals, such as carbon steel[2-5], cobalt[6,7], brass[8,9], aluminum[10] and other alloys[11].

For copper protection, the most widely used inhibitors are BT and TT[12-16]. While these chemicals show an excellent effect on corrosion protection, however a high concentration is needed to achieve a desirable effect, making the process economically and environmentally less desirable. However by adding small amounts of other supplementary chemicals such as salts of weak carboxylic acids, halide ions and other organic materials such as amines, a lower concentration of inhibitor solution with a more pronounced effect is required[17,18].

Investigations show that, inhibitors protect the metal surface through adsorption of inhibitor molecules (through hetro atoms such as Oxygen, Nitrogen and sulfur) on the metal surface[19-22], and it is believed that these additives enhance inhibition performance of inhibitor compounds by helping them to adsorb stronger on the metal substrate[1,6,23,24]. However human and environmental safety is a concern with all various industries involved with the consumption of benzotriazoles. These compounds also may present an environmental problem due to their appreciable water solubility, persistence under environmental conditions, and toxicity to microorganisms and plants[25], so reducing the concentration of these chemicals in solutions while maintaining the inhibition properties is very desirable.

The aim of this study is to investigate the enhancement action and synergistic effect of chemicals, Sodium Benzoate, Potassium Iodide and Thiourea on the corrosion inhibition properties of BT and TT on copper surfaces in acidic solution.

EXPERIMENTAL

In order to find the optimum concentrations of BT and TT, for copper corrosion in acidic media, weight loss measurements were carried out using copper plate with 0.5×70×14mm dimensions dipped in 500 ml of each solution (containing different concentrations of BT and TT) at room temperature for 30 days. Before each experiment, electrodes was abraded with wet SiC paper (grades 600-1200), polished with emery paper to mirror surface, then washed with double distilled water, degreased with acetone, dried and finally immersed in test solution.

Electrochemical measurements were carried out using ZAHNER/ IM6-ex Potentiostat/Galvanostat instrument equipped with three electrode system. Saturated calomel electrode (SCE) was used as reference electrode, two graphite rods as counter electrode and a copper metal mounted in resin with 1cm^2 surface areas, as working one. A fine luggin capillary was placed close to the working electrode to minimize the IR drop. All the chemicals were of analytical grade.

In impedance measurements, the applied frequency ranged from 60 kHz to 10 mHz and impedance data were obtained at the open circuit corrosion potential of the working electrode.

The electrode potential was allowed to stabilize for 30 minutes before starting the experiments. The potential sweep rate was 1 mVs^{-1} which was scanned primarily in the cathodic direction from the corrosion potential and subsequently in the anodic direction.

RESULTS AND DISCUSSION

Weight loss measurements

Immersion test Results for copper, in acidic solution with various concentrations of BT, are given in Figure 1. The data indicate that inhibition actions of the both inhibitors were enhanced as the concentration of inhibitors increased in the solution. Tolyltriazole showed good results in low concentrations as compared to BT, however it may be concluded that a reasonable performance obtained only when a high concentration of inhibitors were used. The corrosion of copper was inhibited at 1200 ppm of BT or at 250 ppm of TT.

Impedance results

Impedance spectra measured at OCP are recorded after 30 min immersion at room temperature. Nyquist diagrams of copper in solutions containing 400 ppm of BT in combination with the additives, sodium benzoate, potassium iodide, and thiourea are given in Figure 2.

Figure 3 shows the result of impedance tests of copper in the solutions containing 200 ppm of TT and individual additives.

The Nyquist plots in the case of copper in the solutions with BT show only one time constant in the range of applied frequency and exhibit a depressed loop which suggest a similar corrosion mechanism. From Figure 2 and Figure 3 it is can be seen that the semicircles which correlated with dielectric properties and thickness of the barrier film, are not well defined. In all cases the length and diameter of the cords which is related to charge transfer resistance, increased after addition of additives then it can be concluded that more resistive films on the copper surface was formed.

Synergistic effect on the corrosion inhibition properties of the inhibitors in combination with each additive was seen. The R_p values obtained in the presence of 400 ppm BT/ TU were 7.18 E4 (10 ppm TU), 90.3

E4 (5 ppm TU) and 2.06 E5 Ω cm^2 (1 ppm TU) and in the presence of 200 ppm TT/ TU were 8.78 E4 (10 ppm TU), 1.08 E5 (5 ppm TU) and 2.50 E5 Ω cm^2 (1 ppm TU). These results indicate that high concentrations of TU have a detrimental effect on the inhibition performance of TT while at low concentrations a synergistic effect is observed. The EIS spectra for copper in the presence of the inhibitors and additives were analyzed by fitting to the equivalent circuit by using Z-view software which is shown in Figure 4. The circuit comprises a constant phase element, a charge transfer resistance and a solution resistance. The AC impedance parameters derived from equivalent circuits are presented in TABLE 1.

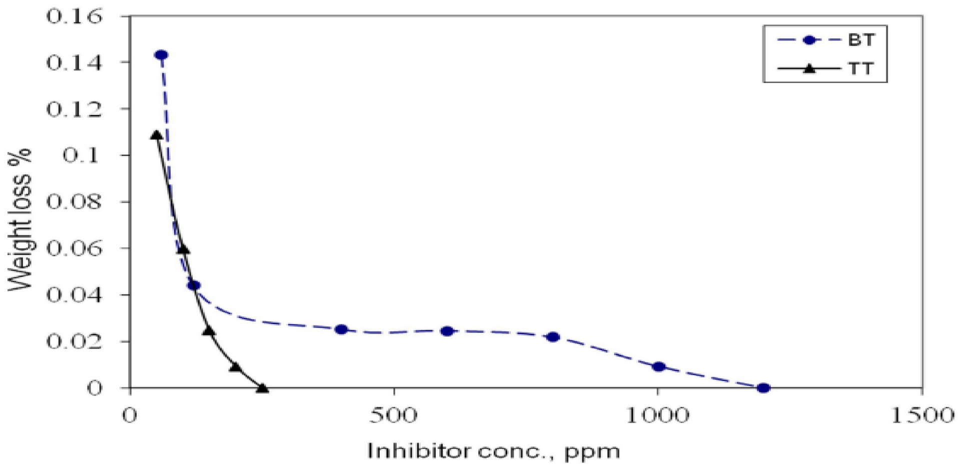

Figure 1 : The weight loss percent of copper specimens vs. BTA and TTA concentration in acidic solution

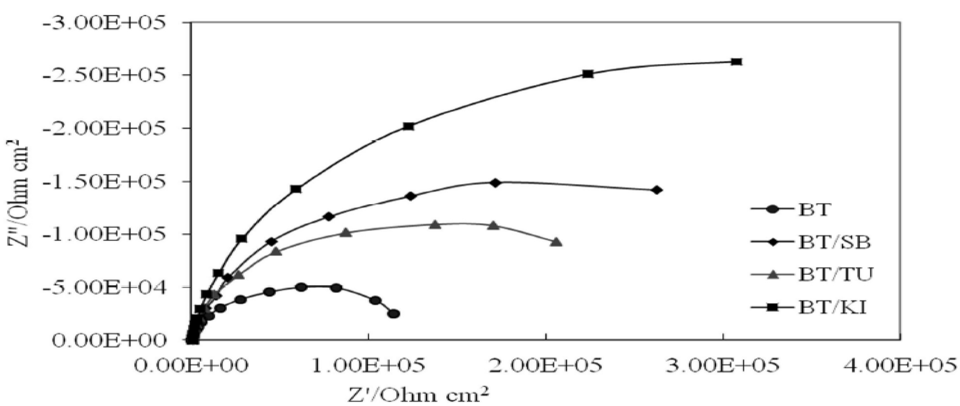

Figure 2 : Nyquist diagram for solutions containing different concentrations of BT

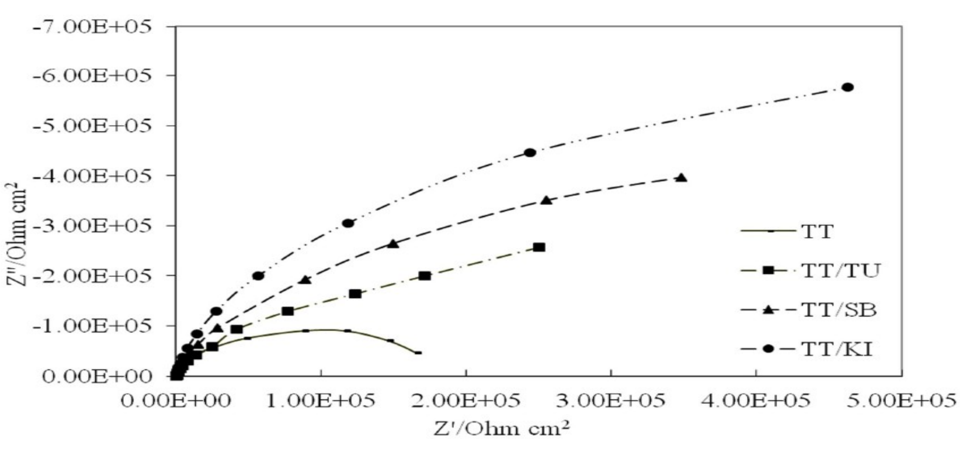

Figure 3 : Nyquist plots for copper in solutions containing 400 ppm of BT with different amounts of additives, SB (a), KI (b), and TU (c)

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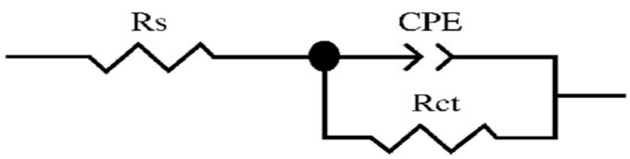

Figure 4 : The equivalent circuit used to fit the impedance spectra

TABLE 1 : The AC impedance parameters derived from equivalent circuits

inhibitor	$R_{ct}\times10^{-5}$/ohm cm^2	C_{dl}/ µF cm^{-2}
BT	1.14	2.411
BT/TU	2.06	2.201
BT/SB	2.63	2.187
BT/KI	3.07	1.819
TT	1.65	1.990
TT/TU	2.50	1.872
TT/SB	3.48	1.643
TT/KI	4.63	1.489

Results show that charge transfer resistance increased after addition of additives and values of double layer capacitance decreased. Formation of protective film on the surface of copper retarded electron transfer from the metal to the solution and cause to increase in the charge transfer resistance. It can be concluded from EIS results that copper corrosion inhibitors have not good performance at low concentrations but incorporation of one of the additives at low concentrations, remarkably improves the inhibition performance of the mixtures.

Figure 5 shows the phase angle between the current and potential. For copper in acidic solution comprising BT, BT/KI, TT and TT/KI, the related values of θ_{max} are 67.6, 78.3, 78.5 and 81.8 respectively and there is just one peak in the plots which represents that the system has one time constant. Appearing the time constant in the phase angle may be due to the formation of thin resistive film on the metal surface. Increasing the values of θ_{max} in the presence of additives is related to the enhancing the inhibitor adsorption on the copper surface which in turn led to an enhanced corrosion protection.

Potentiodynamic polarization studies

Polarization curves were recorded at room temperature with copper having an exposed area of 1cm^2. The working electrode was immersed in test solution (in the presence and absence of optimum concentration of additives) and allowed to stabilize for 30 min.

The cathodic and anodic polarization curves of copper in the acidic solution in the presence of BT or TT with any of additives are shown in Figure 6 and Figure 7 and related electrochemical parameters such as corrosion current density (I_{corr}), corrosion potential (E_{corr}) and Tafel slopes (βa and βc), are presented in TABLE 2. It is evident that in the presence of additives the cathodic and anodic curves were shifted to more positive potential region, which is more pronounced in the case of BT/KI and TT/KI polarization curves and it may be related to more stable protective film on the surface of copper. In all cases at the anodic branch, the current has not increased as the potential goes to more positive values, indicating that the protective film on the electrode surface has a more resistive nature under these conditions.

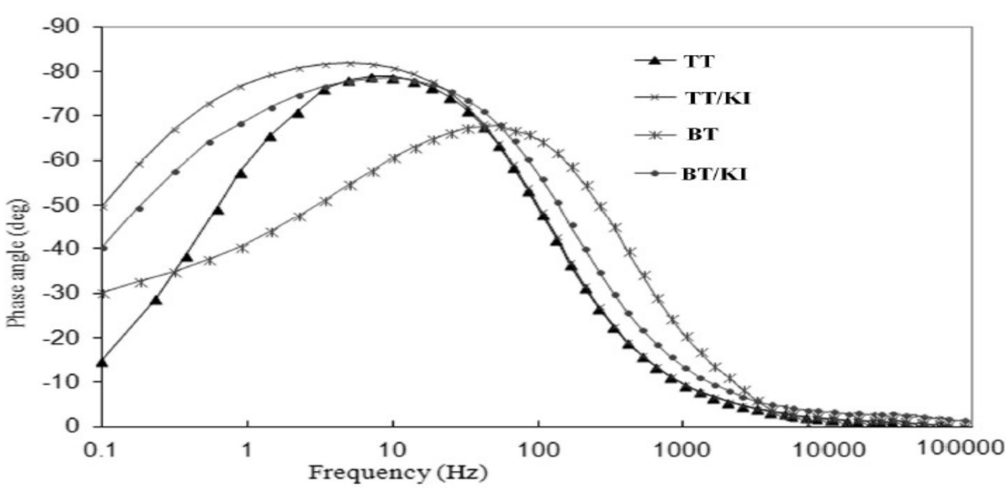

Figure 5 : Phase angle between the current and potential for copper in the presence of inhibitors and additives

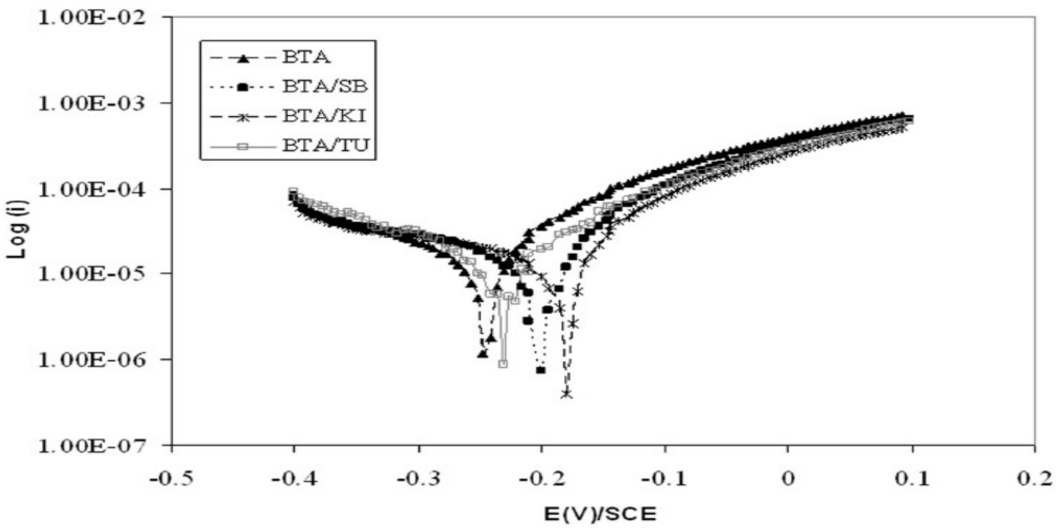

Figure 6 : Potentiodynamic curves for copper in the presence of BT with the three types of additives

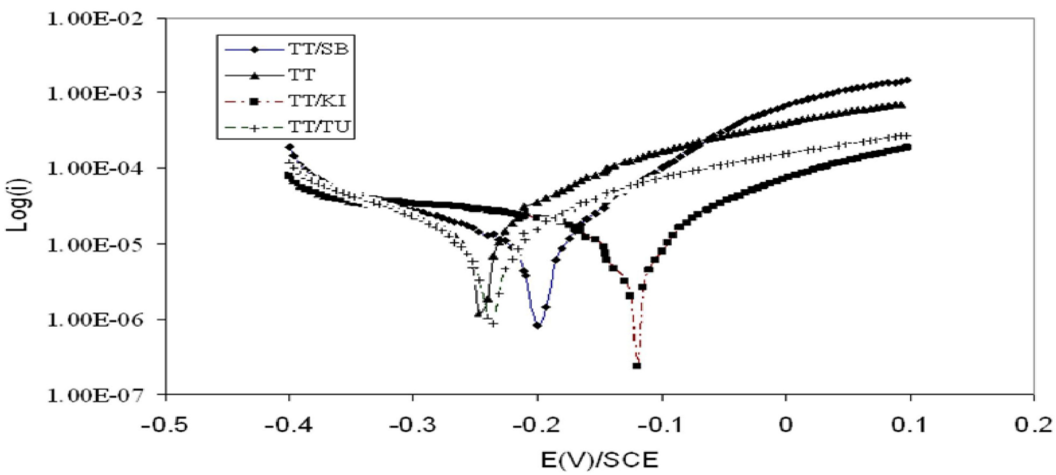

Figure 7 : Potentiodynamic curves for copper in the presence of TT with the three types of additives

TABLE 2 : Electrochemical parameters for copper in the presence of additives and inhibitors

inhibitor	E_{corr} (mV)/SEC	I_{cor} (μA cm^{-2})	β_a (mV dec^{-1})	β_c (mV dec^{-1})
BT	-247	18.73	260	146
BT/TU	-231	11.42	272	172
BT/SB	-207	9.83	293	193
BT/KI	-182	4.37	310	220
TT	-234	16.52	269	168
TT/TU	-226	9.42	283	189
TT/SB	-192	6.14	325	230
TT/KI	-120	2.13	342	246

Open circuit potential measurements

OCP curves for copper in acidic solution containing inhibitors together with complementary additives are presented in Figure 6. All measurements performed during 1800 sec. EIS and Polarization results confirm that the combination show a much better inhibitive performance than that of a sole inhibitor.

The OCP curves follow similar regimes implying that after a few seconds the passivation layer on copper is formed and a full protection has taken place (always the potentials shifted to positive direction). In the case of BT, it is clear that adsorption of this inhibitor on metal surface has been completed after about 300 second’s immersion, but in the solution with additives the full adsorption seen within first seconds. The adsorption of inhibitor/additive combination on the metal substrate caused the formation of a passive layer which enable us to use low concentration of inhibitors (mixing with additives) to protect the metal instead of using higher concentrations of sole inhibitors.

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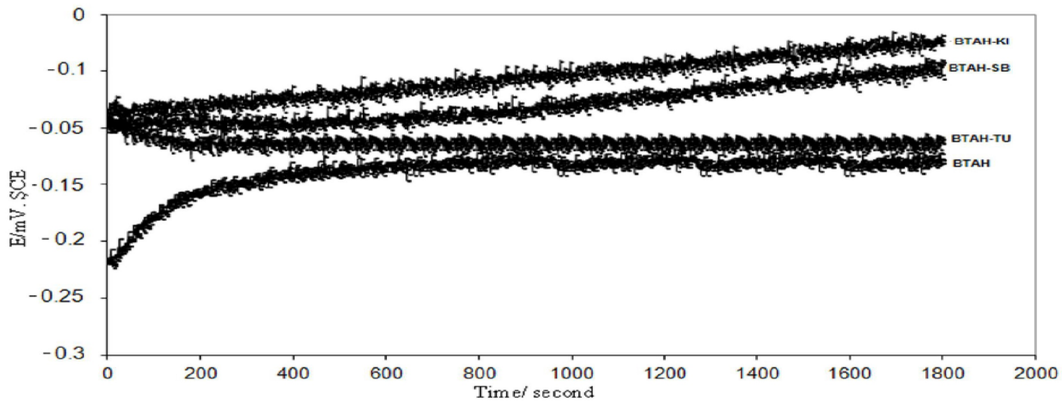

Figure 8 : OCP curves for copper in acid solution with BT and with additives

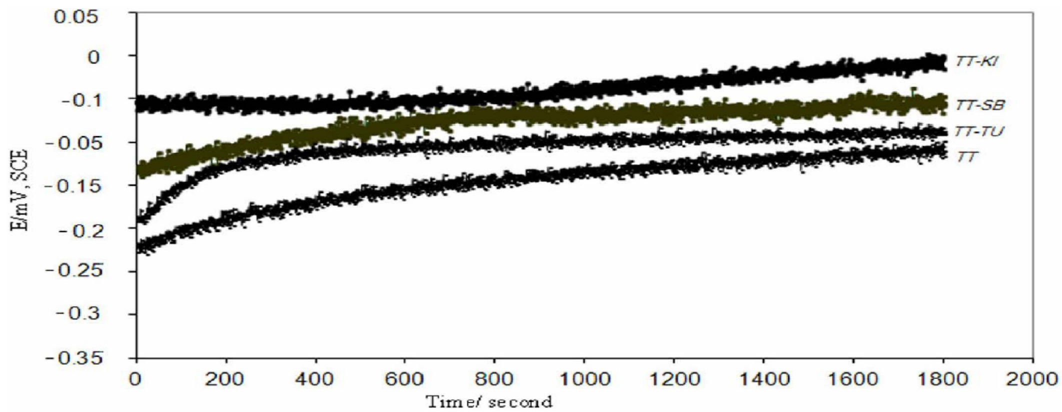

Figure 9 : OCP curves for copper in acid solution with inhibitors TT and with additives

CONCLUSION

- BT and TT are good corrosion inhibitors for copper metal, although increasing the inhibitors concentration cause an increasing in their performance, as indicated by weight loss measurements and EIS curves but higher concentrations of these chemicals rises an economical and environmental safety concerns.
- The efficiency of two tested inhibitors improved significantly after adding any types of investigated chemicals with optimum concentrations of 1ppm TU, 300 ppm KI and 250 ppm SB. However, an optimum mixture of these inhibitors with the proposed additives results in requirement of lower concentrations of inhibitors to reach desired corrosion inhibition efficiency.
- The OCP curves shifted towards more positive potentials after adding these chemicals, implying that after a few seconds the passivation layer on copper is formed and a full protection has taken place.

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