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Corrosion and Inhibition of Cu-Zn Alloys in Acidic Medium by Using Isatin

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The effect of isatin on the corrosion of Cu-Zn alloys in H_2SO_4 and HCl solution has been studied using open circuit potential, potentiodynamic, and electrochemical impedance spectroscopy (EIS) techniques. The addition of increasing concentrations of isatin decreases the corrosion rate, which indicating the corrosion inhibition effect. The adsorption characteristics of isatin on the Cu-Zn alloy surface play a significant role in the inhibition processes. The effect of isatin on the corrosion behavior of Cu-Zn samples I and II (with different composition) was also studied in H_2SO_4 and HCl solutions.

Keywords: Cu-Zn alloy, corrosion, isatin, inhibition

1. INTRODUCTION

The chemical industry employs copper and its alloys extensively for condensers, evaporators, fractionating columns, etc. Copper does not displace hydrogen from acid solution and it is therefore unattacked in non-oxidizing acid environments. Nevertheless, most acidic solution contains dissolved air that enables some corrosion to take place. Many organic molecules are used to inhibit copper corrosion [1-6]. The primary step in the action of organic corrosion inhibitors in acid solutions is usually adsorption at the metal-solution interface. The adsorption process depends on the electronic of the molecules (adsorbate), the chemical composition of the solution of the solution, nature of the metal surface, temperature of the reaction and on the electrochemical potential at the metal-solution interface [7]. The adsorption requires the existence of attractive forces between the adsorbate and the metal. According of the type of forces, adsorption can be physisorption or chemisorption or a combination of both [8]. Physisorption is due to electrostatic attractive forces between inhibiting organic ions or dipoles and the electrically charged surface of the metal. Chemisorption is due to inter action between unshared electron pairs or π electrons with the metal in order to form a coordinate type of bond. It may take place in presence of heteroatoms (P, Se, S, N, O), with loon pair of electrons and/or aromatic rings in the adsorbed molecules [9-13].

Isatin is an indole derivative having tow carbonyl groups in the 2 and 3 positions. The carbonyl group in the 3-position behaves like a ketone that is very reactive; the other has amidic behavior [14]. Infrared evidence supports the following structure for isatin and gives no evidence for the enol form [15]. The objective of the present work is to study (1) Tthe stability of the passive film under different conditions, (2) The effect of isatin as corrosion inhibitor of Cu-Zn alloy in acidic medium using electrochemical methods and EIS techniques, (3) The role of these anions improving the passive film resistance to the corrosion caused by acidic medium, (4) The effect of Al content on the stability of protective film towards corrosion.

2. EXPERIMENTAL PART

Experiments were carried out in H_2SO_4 and HCl solutions in absence and presence of different concentrations of isatin. All solutions were prepared from double distilled water. A. R. chemicals and new polished electrodes were used for each run. All experiments were carried out at room temperature (25°C). All solutions were used under purified nitrogen gas. Two Cu-Zn samples were used in the present work as working electrodes. The composition (wt %) of sample (I) is 78% Cu, 20% Zn and 2% Al. The composition of the second sample (II) is 69% Cu and 31% Zn. The ingots were machined in the form of short rods, each 20 mm in length and 5 mm in diameter. Each working electrode was constructed and treated following the procedure described previously [16]. The required pH was achieved by a dropwise addition of standard NaOH solutions. A Lseibolo Wien pH meter was used to measure the pH values. A Pt sheet was used as a counter electrode. The potential was measured against Ag/AgCl electrode. The polarization measurements were run on a computerized potentiostat (Radiometer model VoltaLab 40) and VoltaMaster 4 software.

3. RESULTS AND DISCUSSION

The open circuit potentials of the two Cu-Zn samples immersed in H_2SO_4 or HCl solutions in the different concentrations were followed as a function of time, till the steady state values were attained. The steady state potential $E_{s.s}$ values approached from more negative values with increasing H_2SO_4 or HCl concentrations indicating the destruction of pre-immersion passive film found on the Cu-Zn surfaces. Fig. 1 illustrates the straight line relationship between $E_{s.s}$ and [acid] which satisfies the following equation:

$$E_{s.s} = a - b \text{ Log [acid]}$$

Symbols a and b are constants dependent upon the composition of the Cu-Zn alloy. The negative shift in $E_{s.s}$ indicates that H_2SO_4 or HCl accelerate the anodic (metal dissolution) reaction. This could be attributed to direct participation of adsorbed Cl^- or SO_4^{2-} ions in ionization of the alloy.

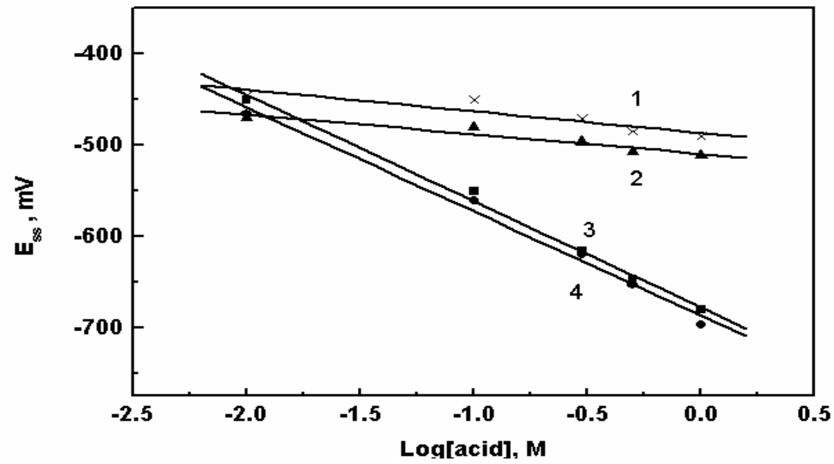


Figure 1. Variation of steady state potential ($E_{s.s}$) with the concentration of different acids: 1) sample I in H_2SO_4, 2) sample II in H_2SO_4, 3) sample I in HCl, and 4) sample II in HCl.

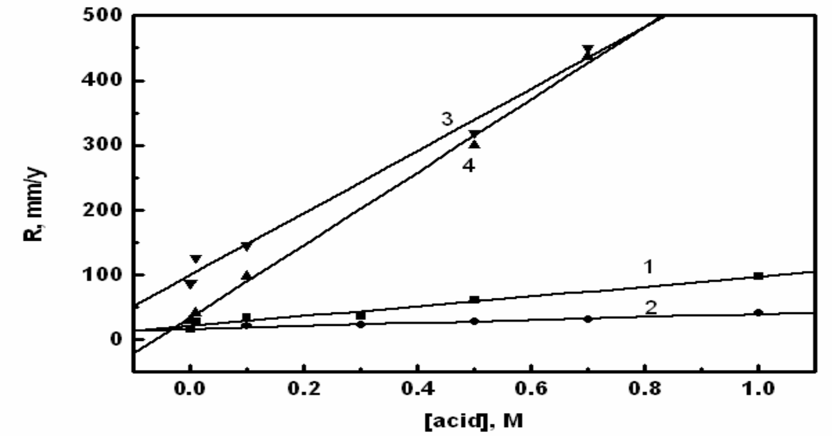


Figure 2. Corrosion rate as a function of acids concentrations: 1) sample I in H_2SO_4, 2) sample II in H_2SO_4, 3) sample I in HCl and 4) sample II in HCl.

Therefore, one can conclude that the corrosion of Cu-Zn in H_2SO_4 or HCl solutions is determined by polarization of the anodic controlling reaction, i.e., the corrosion process is anodically controlled. The data in Fig. 1 show that the steady state potentials of sample II are more negative than those of sample I and $E_{s.s}$ in presence of HCl is more negative than that in presence of H_2SO_4. These results indicate that sample II suffers more corrosion than sample I. This observation may be attributed to the relatively high resistance of the sample I due to the presence of Al. The potentiodynamic polarization curves for samples (I, II) in different concentrations of H_2SO_4 or HCl solutions was measured. Figure 2 indicates that an increase in H_2SO_4 or HCl concentrations increases the corrosion rate for the two samples. The adsorbed Cl^- ions participate directly in the ionization of the metal atoms. The corrosion resistance of the alloy samples increase in the order: I > II, this sequence can be argued to the presence of Al in sample I. According to Pourbaix diagram for Al [17], a stable Al_2O_3 passive film formed in neutral medium (pH=4-8) and in the potential range (-1.8 to 1.1 V). Figure 2 also indicates that corrosion resistance H_2SO_4 > HCl this sequence can be argued to the higher aggressive effect of chloride ions relate to sulfate ions.

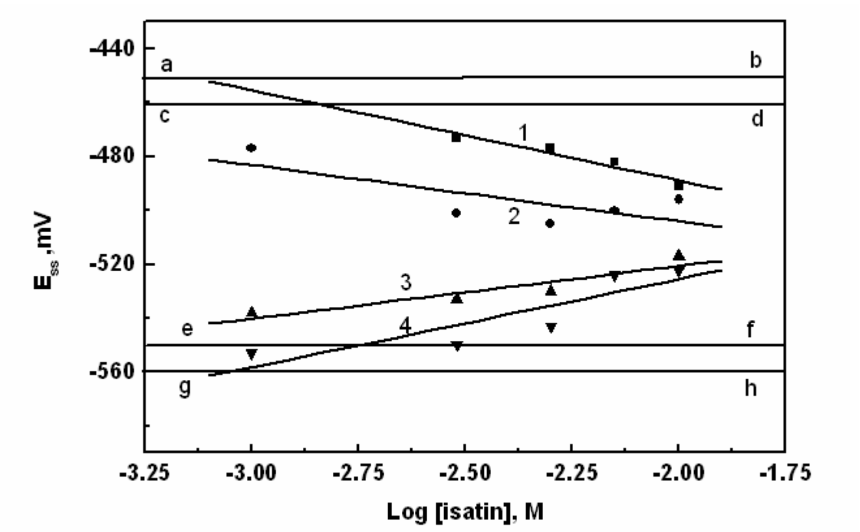


Figure 3. Variation of steady state potential ($E_{s.s}$) in the concentration 0.1 M of acids and different concentration of isatin: 1) sample I in H_2SO_4, line a-b 0.1 M H_2SO_4 2) sample II in H_2SO_4, line c-d 0.1 M H_2SO_4, 3) sample I in HCl, line e-f 0.1 M HCl and 4) sample II in HCl, line g-h 0.1 M HCl

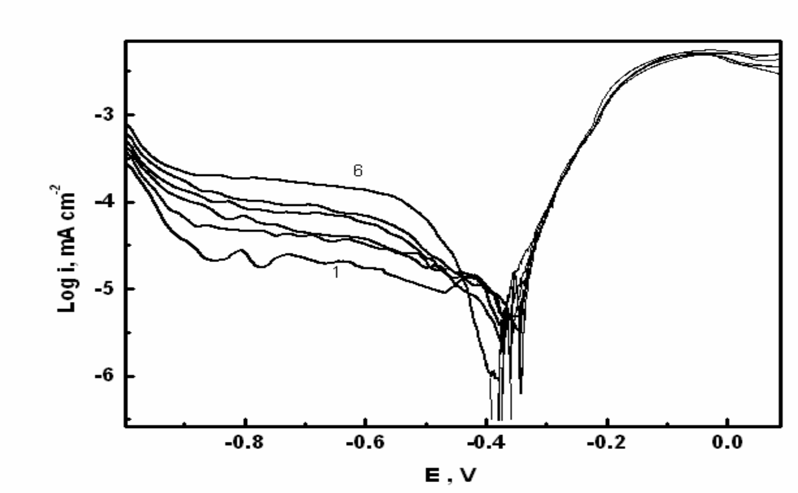


Figure 4. Polarization curves for sample I in 0.1 M HCl solution in the presence of different concentrations of isatin: 1) 0.0, 2) 0.0001, 3) 0.0003, 4) 0.0005, 5) 0.0007 and 6) 0.001 M

Figure 3 manifests the variation of $E_{s.s}$ of the two Cu-Zn alloy samples in 0.1 M H_2SO_4 or HCl solutions containing different concentrations of isatin. It is worthy to note that $E_{s.s}$ shift to more positive with increasing the concentration of isatin in HCl but to more negative in H_2SO_4, according to the following equation:

$$E_{s.s} = A + B \text{ Log [isatin]}$$

Symbols A and B are constants depend on the composition of the alloy. Such behavior could be related to an increase in the anodic polarization potential in HCl and cathodic polarization potential in H_2SO_4 which reflect in an increase in the inhibition efficiency of isatin (as a result of increasing its concentration). Therefore, one concludes that the corrosion of alloys in the presence of isatin is under anodic control in HCl and under cathodic control in H_2SO_4.

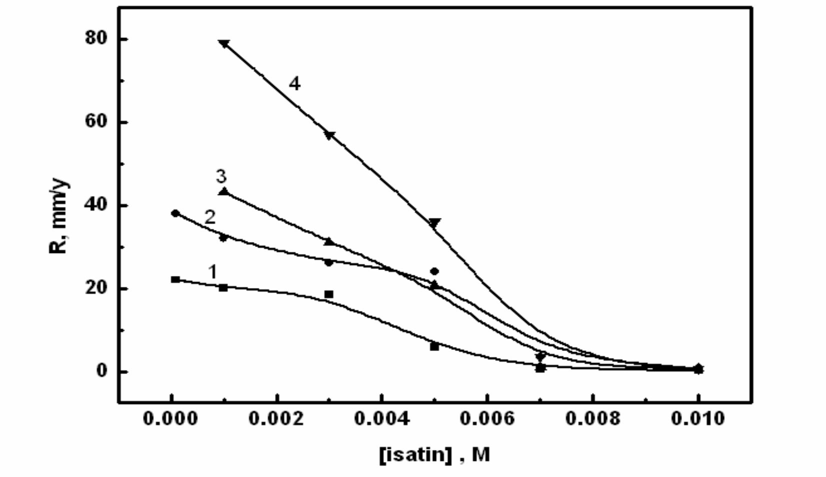


Figure 5. Corrosion rate for different samples in 0.1 M of different acids as a function of inhibitor concentrations: 1) sample I in H_2SO_4, 2) sample II in H_2SO_4, 3) sample I in HCl and 4) sample II in HCl.

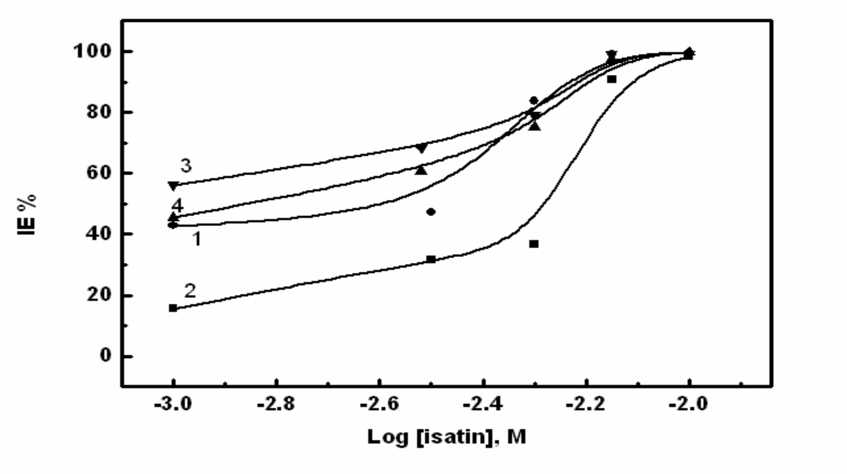


Figure 6. Inhibition efficiency for different samples in 0.1 M of different acids as a function of inhibitor concentrations: 1) sample I in H_2SO_4, 2) sample II in H_2SO_4, 3) sample I in HCl and 4) sample II in HCl.

The effect of adding increasing amounts of isatin to 0.1 M H_2SO_4 or HCl on the potentiodynamic polarization curves was investigated (Fig. 4, as example). At potentials of about -550 mV with respect to E_{corr} a sharp current increase arising from chathodic hydrogen is observed in H_2SO_4. Furthermore as the concentration of isatin increases E_H- shifts cathodically. This effect can be interpreted by considering that the isatin is like other adsorption inhibitors, which should adsorb at the metal-solution interface. This limits the accessibility of the surface to the reacting ions H_3O^+ and could cause an increase in the hydrogen overpotential. Finally because the cathodic Tafel slopes for hydrogen reduction (b_C) in were essentially unaffected this means that the inhibitor did not affect the hydrogen reduction mechanism [18]. Figure 5 indicates that the increasing of isatin concentration leads to decreasing the corrosion rate. This result is suggesting that isatin is acting as corrosion inhibitor for the two alloys in H_2SO_4 or HCl solutions. The calculated inhibition efficiency (IE) from the corrosion rate can be indicated in Fig. 6. The inhibition efficiency of isatin increases with increasing of its concentration. The inhibiting effect of isatin can be explained on the basis of the competitive adsorption between its molecules and the aggressive SO_4^{2-} or Cl^- anions on the passive electrode surface and thus retards their corresponding destructive action [19]. The inhibitive anions may be incorporated into the passive layer on the alloy surface, forming an improved stability against the aggressive ions. The increase of the isatin content in the passive layer leads to a significant increase in corrosion resistance [20,21]. Figure (7) shows that the protective property of isatin is directly dependent on the pH of the solution, an increase in the pH (in 0.01 M isatin and 0.1 M H_2SO_4 pH is 1.6) is accompanied by increased in the corrosion rate, i.e. decrease the stability of the passive film obtained specially in alloy II .

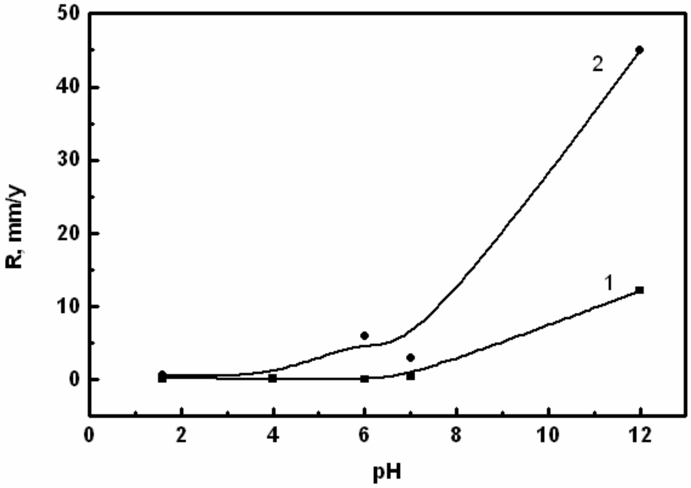


Figure 7. Dependence of corrosion rate on pH: 1) sample I in 0.1 M H_2SO_4 and 0.01 M isatin, 2) sample II in 0.1 M H_2SO_4 and 0.01 M isatin.

Figure 8 shows the impedance complex diagrams (Nyquist plot) of sample I and II in 0.1 M H_2SO_4 or HCl solutions. The impedance diagram gave a semicircle type appearance, indicating that the corrosion of alloys is mainly controlled by charge transfer process. The impedance measurements were carried out at the open circuit potential, i.e. at the corrosion potential (E_{corr}). The impedance complex diagrams of samples (I, II) in 0.1 M of H_2SO_4 or HCl in presence of isatin was shown in Fig. 9. The impedance diagrams in Figs. 8 and 9 show that the charge transfer resistance of different alloys in 0.1 M of H_2SO_4 or HCl increases in the presence of isatin. Electrochemical theory shows that the reciprocal of the charge transfer resistance is proportional to the corrosion rate [22]. The corrosion rate of Cu-Zn alloys in 0.1 M of H_2SO_4 or HCl is higher than that in presence of isatin. The corrosion rate in 0.1 M HCl in the presence of 0.01 M isatin is higher than that in 0.1 M H_2SO_4 in the presence of the same concentration of isatin. This indicates that HCl is more efficient than H_2SO_4; this is in good agreement with the d.c. polarization results.

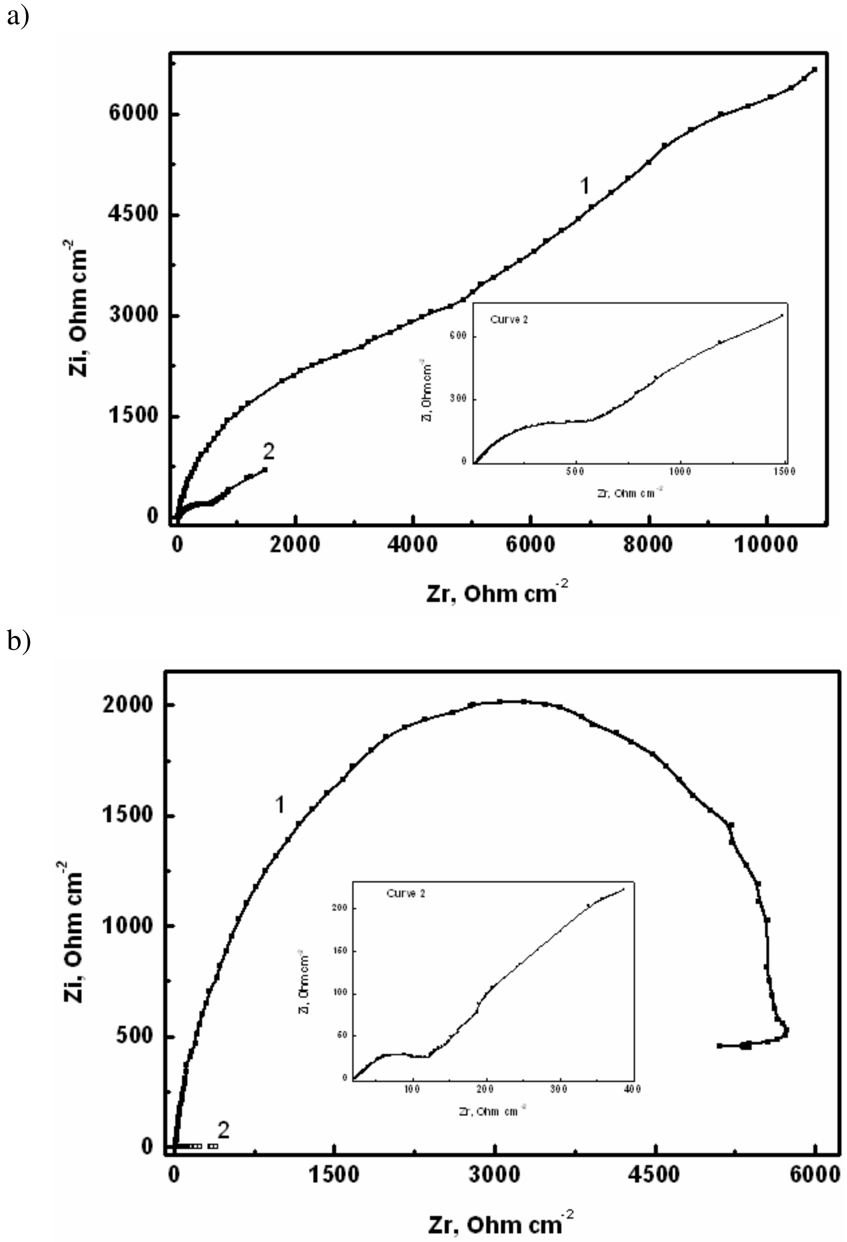


Figure 8. a) Nyquist plot for sample I in 0.1 M of:: 1) H_2SO_4 and 2) HCl. b) Nyquist plot for sample II in 0.1 M of:: 1) H_2SO_4 and 2) HCl

In the ω versus θ Bode plots, there is one phase maximum (Fig. 10, as example), i.e. one relaxation process. This result indicates that there are one charge transfer processes taking place at the alloy-electrolyte interface. This process is due to the diffusion of different component (SO_4^{2-}, Cl^- and isatin) at the alloy-electrode interface. The Bode plot (ω versus |Z|) shows the presence of inhibitor leads to decreasing of impedance values, which may be due to the adsorption of different corrosion products and inhibitor species (isatin) on Cu-Zn alloy surface. The comparison of impedance in Bode plot for samples I or II (Fig. 10, as example) indicates that it is increase in the order: I > II, this sequence can be argued to the presence of Al in sample I as discussed above.

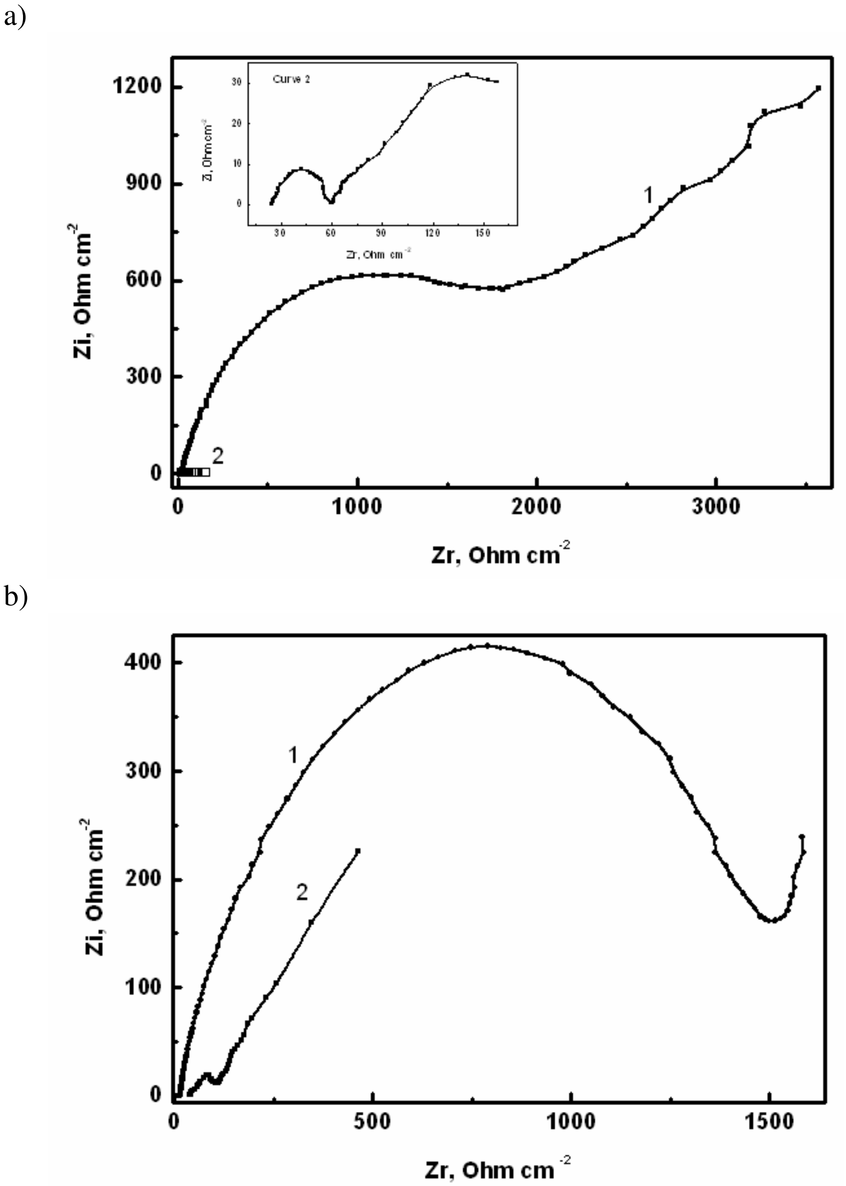
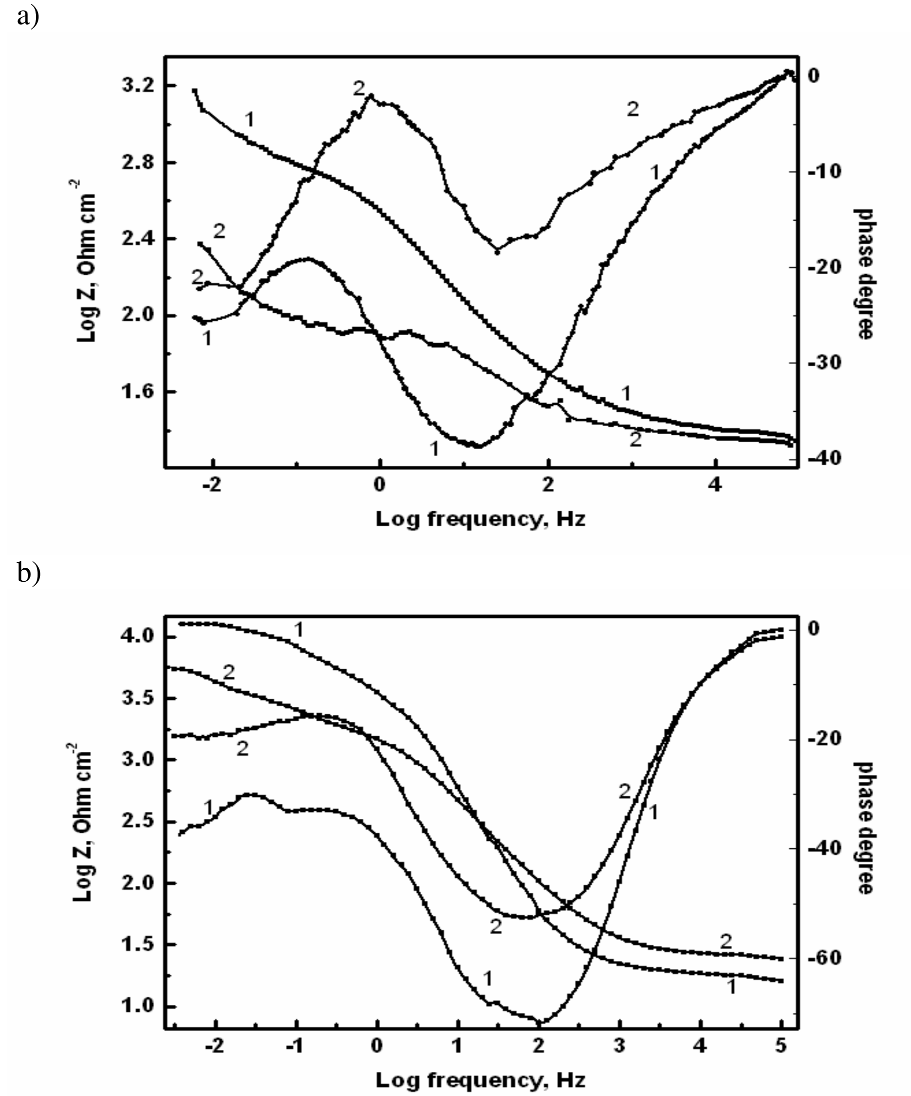


Figure 9. a) Nyquist plot for sample I in: 1) 0.1 M H_2SO_4 and 0.007 M of isatin and 2) 0.1 M HCl and 0.007 M of isatin. b) Nyquist plot for sample II in: 1) 0.1 M H_2SO_4 and 0.01 M of isatin and. 2) 0.1 M HCl and 0.01 M of isatin.

4. CONCLUSIONS

Isatin acts as inhibitors for the corrosion of the two alloy samples (I, II) in 0.1 M H_2SO_4 or HCl. The inhibition efficiency increases with the increasing of the concentration of isatin. The presence of isatin inhibits the corrosion of alloy samples cathodically in 0.1 M H_2SO_4 or anodically in HCl solutions in the order: H_2SO_4 > HCl. The inhibition is due to the adsorption of the isatin molecules on the sample surface.



Figrue 10. a) Bode plot for: 1) sample I in 0.1 M HCl and 2) sample I in 0.1 M HCl and 0.01 M isatin. b) Bode plot for: 1) sample I in 0.1 M H_2SO_4 and 2) sample I in 0.1 M H_2SO_4 and 0.007 M isatin.

References

1. D.Altura, K. Nobe, *Corrosion* 28 (1972) 345.
2. R.J.Chin, D.Altura, K. Nobe. *Corrosion* 29 (1973) 185.
3. S.L.F.A. Da costa, S.M.L. Agostinho, *Corrosion* 35 (1989) 472.
4. J.B. Cotton, PROC. 2nd Int. Conger. Met. Corrosion, New York. 1963 NACE, Houston. Texas, 1966. p. 590.
5. G. Schmitt, *Brit. Corrosion. J.* 19 (1984) 165.
6. V. Molokanov, G. Moretti, G. Quartarone, A . Zingales, *Corrosion* 54 (1998) 135.

7. G. Trabanelli, in: F. Mansfeld (Ed). Corrosion, Mechanism, Marcel Dekker, New York. 1987, p. 119.
8. D. P. Schwensberg, G. A . Nanayakkara, D. A. Steinert. *Corrosion. Sci.* 28 (1988)33
9. M. Ohsawa, W. Sue Taka, *Corros. Sci.* 19 (1979) 709.
10. J. Penninger, K. Wipperrmann, J. W. Schultze, *Werkst. Und Korros*. 38 (1987) 649.
11. J. W. Schultze, K. Wippermann, *Electrochim. Acta* 32 (1987) 823.
12. H. A.El-Rahmann, *Corrosion.* 47 (1991) 424.
13. M. M. Singh, R.B.Rastogi, B. N. Upadhyay, *Corrosion* 50 (1994) 620.
14. R. Fusco, V. Rosati, G. Bianchetti, in: Chemica Organica. First ed., L. G Guadagni, Milano, 1969. p.607.
15. D. G. O›Sullivan, P. W. Sadler*, J. Chem. Soc*. (1956) 2202.
16. S. A. M. Refaey, *Appl. Surf. Sci.,* 157(2000)199
17. M. Pourbaix, Atlas of Electrochemical Equilibria, Pergamon, Oxford (1966).
18. E. Mattson, J. O. M. Bockris, *Trans. Faraday Soc*. 55 (1959) 1586.
19. E. W. Abel, comprehensive inorganic chemistry, J. C. Bailar et al., eds. (oxford, UK. Pergamon Press, 1965) P. 124.
20. V. Mitrovic-Scepanovic, R. J. Brigham, *Corros. Sci*., 52(1)(1995) 23
21. S. A. M. Refaey, *Appl. Surf. Sci.,* 240 (2005) 396
22. D.Hladky, L. M. Callow, J. L. Dawson, *Br. Corrosion. J*., 15, (1980) 20