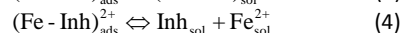
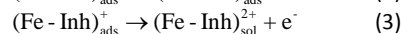
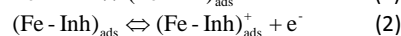
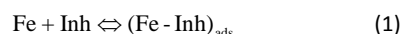


## Anodic dissolution mechanism for iron in presence of pyridine-2-thiol in 0.1 M HCl

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The use of organic compounds as corrosion inhibitors may be the main choice to reduce the corrosion rate of alloys in acidic media. Presence of unique atoms such as N, O and S in heterocyclic compounds determines both efficiency and adsorption mechanism. In recent years, the quantum chemical method has presented an insight toward identifying the relation between molecular structure of inhibitors and their adsorption mechanism. However, it is not capable method to describe the dissolution mechanism of metals. In this way, the electrochemical methods can be valuable techniques to recognize mechanism of dissolution. Consequently, the aim this work is devoted to study the iron dissolution behavior in the presence of 2-pyridyl disulfide (see Fig.1) in 0.1 M HCl using electrochemical techniques. CK15 mild steel was selected as working electrode and saturated calomel and platinum wire as reference and counter electrodes. At the first, potentiodynamic polarization of mild steel in inhibited solution reveals a considerable decrease in anodic and cathodic Tafel slopes in comparison with the uninhibited solution (see Fig 2). Meanwhile, both anodic and cathodic current densities have been decreased in the presence of 2PD, leading to a significant decrease in corrosion rate. Focusing on a noticeable decrease in Tafel slopes, it may be claimed that present compound affect the both anodic dissolution of iron and hydrogen evolution. Change in anodic Tafel slope is observed in higher noble potentials so that this slope is similar to the blank solution one. This phenomenon refers to the detachment of inhibitor molecules from the surface, resulting in no effect on iron dissolution. While no change in Tafel slope in cathodic branch of the polarization curve can be attributed to the presence of inhibitor onto the surface. The EIS recordings at corrosion potentials ( $E_{\text{corr}}$ ) for inhibited and uninhibited solutions exhibit a typical impedance behavior including a depressed semicircle with only a time constant in whole frequencies domain (30000 to 0.01 Hz). To better detect the anodic and cathodic reactions, EIS tests were run at -100 and +100 mV overpotential with respect to  $E_{\text{corr}}$ . In the case of inhibited solution with +100 mV DC offset, the total impedance intensely decreases and impedance plot shows two time constants so that an inductive loop is observed at lower frequencies (Fig. 3). At -100 mV overpotential, the total impedance has a larger value in comparison with corresponding value in anodic overpotential, considering that no inductive loop tail is observed in Nyquist plot. It is reported that low-frequency inductive loops in the

impedance response can be attributed to Faradaic reactions that involve adsorbed intermediate species. It may be recommended that sulfur ligands of the structure of inhibitor can form charge-sharing bonds (considering  $\Delta G_{\text{adsorption}}$  of -44.8 kJ/mol calculated by Langmuir adsorption isotherm) with iron at surface that causes a weakening in the metal-metal bonds, which leads to a lowering of the activation energy barrier for the passage of a metal atom to the solution, apparently due to change in the symmetric factor,  $\alpha$ , in Butler-Volmer equation. According to above discussion, the following mechanism may be proposed for iron dissolution in presence of 2PD:



Finally, it can be say that the present inhibitor molecule reduces the corrosion rate by decreasing the surface active area by forming physisorption of phenyl rings with Fe atom at surface. Although, chemical bond of sulfur ligands with Fe atom that facilitate anodic dissolution of iron, cannot be ruled out.

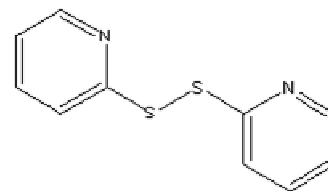
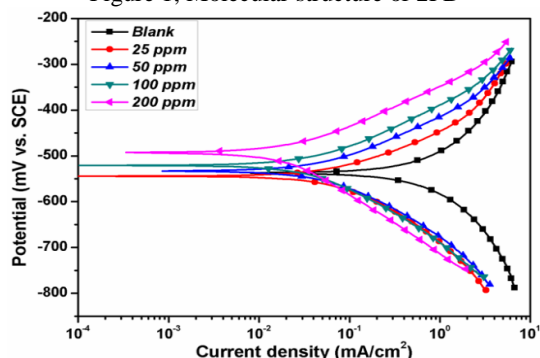
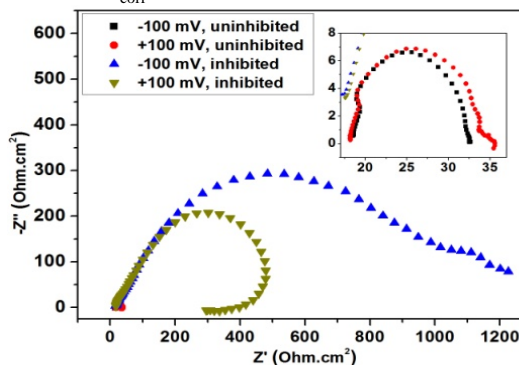


Figure 1, Molecular structure of 2PD

Figure 2, Potentiodynamic polarization of mild steel in the potential range of -250 to 250 mV with respect to  $E_{\text{corr}}$  with scan rate of 60 mV/min.Figure 3, Nyquist plot at -100 and +100 mV DC offset with respect to  $E_{\text{corr}}$