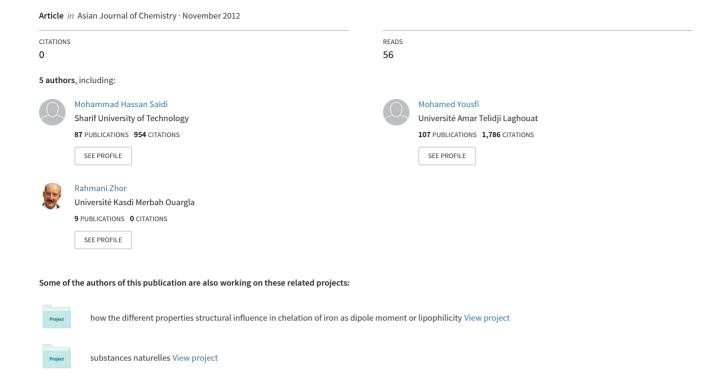
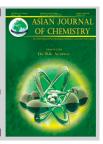
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Enhancement of the Inhibitor Efficiency of 4-Phenyl-1,2-dithiol-3-thione on Corrosion of Mild Steel for 20 % Sulphuric Acid

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Subtituted 4-phenyl-1,2-dithiol-3-thione (PDTT) synthesized and tested as inhibitors for the corrosion for mild steel in the presence of oxygen by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) technique in 20 % H_2SO_4 at 25 °C. This organic compound inhibits the acidic corrosion even at low concentration. The results obtained show that these sulfur compound is good inhibitors and are in good agreement. Polarization curves indicate that 4-phenyl-1,2-dithiol-3-thione is a cathodic inhibitor and able to reduce the corrosion current, obtained from electrochemical impedance spectroscopy measurement, were analyzed to model the corrosion inhibition process throught appropriate equivalent circuit model. The adsorption of 4-phenyl-1,2-dithiol-3-thione on the steel surface in 20 % H_2SO_4 solution, obeys to Langmuir's isotherm with a very hight negative value of the free energy of adsorption ΔG°_{ad} .

Key Words: Acid, Corrosion, Inhibition, Dithiole thione, Mild steel, Electrochemical impedance spectroscopy, Adsorption.

INTRODUCTION

Organosulfur derivatives are exogenic compounds known as antioxidants in varoious therapeutic applications. Among these sulfur compounds, 1,2-dithiol-3-thiones (dithiolethiones) are extensively investigated owing to their chemopreventive effect in numerous condition, prevention of hepato-, nephro-, tenotoxicity, neuroprotection, effect in inflammation, cerebal and cardiac, ischemia and cancer chemoprevention¹. A number of derivatives of 3*H*-1,2-dithiol-3-thiones have been shown to induce phase II detoxification enzymes².

First quantitative structure-activity relationships (QSAR) between electrophile detoxication properties of 1,2-dithiol-3-thiones, for exemple the use of Hammet electronic parametres δ , shows that electronic effect of the substituent may play an important role in DNA-binding of ligands³ and determine their water/n-octanol partition coefficient, log P. A very significant linear property was found with some disubstituted derivatives. It was found that the less lipophilicity dithiolethiones were the most active⁴.

1,2-Dithiol-3-thiones are five-membered cyclic sulfurcontaining compounds with antioxidant chemotherapeutic and chemoprotective activities these compound are used in different domaine, such as, oltipraz a member of a class of dithiol thione is induced phase 2 enzyme response conserved in cells lacking mitochondrial DNA⁵, then sulfarlem is widely used in human therapy for its choleretic, sialogogic properties and as cytoprotective agent in lung precancerous lesions prevention in smokers⁶ and finally 3-methylthio-1,2-dithiolium cation was aesily reduced in DMF at a mercury electrode⁷.

Acid solutions are used for the removal of undesirable scale and rust in many industrial processes8. It is well known that sulphuric acid used for the removal of undesir-able scale and rust in several industrial processes trigger corrosion of puremetals and alloys⁹. Aggressive acids predominantly sulphuric acid are widely used for industrial and some specific treatments (e.g. chemical cleaning pickling) of mild steel most especially when intended for hot-dip galvanizing. However, these acids are known to cause severe corrosion problems¹⁰. In order to minimize the loss of mild steel, the use of inhibitors is one of the most practical methods for protection against metallic corrosion, especially in acidic media. Many organic compounds containing polar functions such as oxygen, nitrogen, sulphur and phosphorus in their molecular structures have been used as corrosion inhibitor for metal¹¹⁻²¹. While sulphur containing inhbitors exert their best efficiency in sulphuric acids²²⁻²⁴ such as sulphoxides, sulphide and thioureas²⁵. Inhibitors find application in pickling cleaning and acid descaling processes in general organic compounds such as, amines, acetylenic alcohol, heterocyclic compounds etc., have found use as inhibitors in industrial applications²⁶.

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The primary step in the action of organic corrosion inhibitors in acid solutions is usually adsorption at the metalsolution interface. The adsorption requires the existence of attractive forces between the adsorbate and the metal. According to the type of forces, adsorption can be physisorption, chemisorption or a combination of both. 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 interaction between unshared electron pairs or π -electron of the adsorbate with the metal in order to form a coordinate type of bond. It may take place in presence of heteroatom (P, Se, S, N, O), with lone-pair electrons²⁷, functional groups, steric factors, aromacity, electron density at the donor atoms and (π) orbital character of donating electrons²⁸ and also on the electronic structure of the molecules^{29,30}. According to this mechanism, a reduction of either the anodic or the cathodic reaction or both arises from the adsorption of inhibitor on the corresponding active sites. The electronic characteristic of the molecules (adsorbate), the chemical composition of the solution, the nature of the metal surface, the temperature of the reaction and the electrochemical potential at the metal-solution interface determine the degree of adsorption and hence the effectiveness of

The compound 4-phenyl-1,2-dithiol-3-thione (PDTT), is an example of a new class of corrosion inhibitors (Fig. 1). The aim and the objective of the present work is to investigate the efficiency of 4-phenyl-1,2-dithiol-3-thione as corrosion inhibitors of mild steel X52 in 20 % sulphuric acid, in order to study the influence of a sulfur atom and aromaticity, in the part of the molecule.

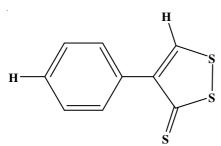


Fig.1. Molecular structure of the 4-phenyl-1,2-dithiol-3-thione (PDTT)

EXPERIMENTAL

The investigated 4-phenyl-1,2-dithiol-3-thione (PDTT) was synthesized in the laboratory according to described procedure³⁰ and was purified and analyzed by IR and measure point of fusion before used. The concentration range employed was 25×10^{-3} mM to 126×10^{-3} mM.

Corrosion tests have been carried out on electrodes of mild steel. Steel stips containing percentage composition of (in wt. %) C: 0.1038, Mn: 0.971, S: 0.0021 and remainder iron was used, as the working electrode for the electrochemical studies. The surface prepration of the specimens was carried out by grinding with emery paper grade 400 and 1200 they were dried at room temperature before use. The acid solution (20 % $\rm H_2SO_4$) was prepared by dilution of analytical grade 98 % $\rm H_2SO_4$ with distilled water.

Polarization curves were conducted at 25 ± 1 °C using an electrochemical measurment system controlled with Tacussel Radiometer PGP201 corrosion analysis. Electrochemical experiments were carried out in a glass cell with acapacity of 500 mL. A saturated calomel electrod (SCE) as a reference electrode. A platinum electrod were used as a counter. All potentials are reported vs. SCE.

For Tafel polarization technique and electrochemical impedance spectroscopy (EIS), the working electrode was in the from of a disc cut from mild steel under investigation and was embedded in a Teflon rod with an exposed area of 1.0 cm². A calomel electrod was placed close to the working electrode to minimize ohmic resistance. All test solution were aerated in the cell, the test solution was mixed with a magnetic. The anodic and cathodic polarization curves were recorded by a constant sweep rate of 0.5 mV s⁻¹.

Electrochemical impedance spectroscopy (EIS) was coducted in an electrochemical measurement system (Voltalab40) which comprises a PGZ301 potentiontat and Tacussel Frequency Responce Analyzer.

A personal computer and VoltaMaster 4 software and pusing a double glass cell equipped with a thermostated cooling condenser. The solution volume was 500 mL. An ac sinusoid \pm 10 mV was applied at the corrosion potentials (E_{corr}) over a frequency rang of 10⁵ Hz-10⁻³ Hz with ten point par decade was employed. All tests were perfoormed at 25 \pm 1 °C Nyquist polts were obtained from these experiments.

RESULTS AND DISCUSSION

Polarization measurments have been carried out in order to gain knowledge concerning the kinetics of the anodic and cathodic reactions. Polarization curves of the mild steel in 20 % $\rm H_2SO_4$ solutions without and with addition of different concentrations of PDTT are shown in Fig. 2. The anodic and cathodic current-potential curves are extrapolated up to their intersection at a point where corrosion current density (i_{corr}) and corrosion potential (E_{corr}) are obtained E_{corr} 0. Table-1 shows the electrochemical kinetic parameters (E_{corr} 1. Table-1 shows solution without and with different concentration of the investigated (PDTT). The E_{corr} 1 values were used to calculate the inhibition efficiency.

The inhibition efficiency, E (%) (listed in Table-1), is calculated by the following expression³¹:

$$E (\%) = \left[1 - \left(\frac{i_{corr}}{i_{corr}^{\circ}}\right)\right] \times 100 \tag{1}$$

where i_{corr} and i^{o}_{corr} are the corrosion current densities in the presence and absence of the inhibitor in the solutions, respectively.

As was expected cathodic reactions of carbon steel electrode corrosion were inhibited with increase of the synthesized surfactant concentration. This result suggests that the addition of the synthesized inhibitors reduces anodic dissolution and also retards the hydrogen evolution reaction²², the best inhibition efficiency was about 96.95 % at concentration 126×10^{-3} mM. It can be seen that the corrosion rate decreased and inhibition efficiency (E %) increased by increasing inhibitor concentration,

0.101

0.126

92.27

96.65

MEASUREMENTS FOR MILD STEEL IN 20 % H ₂ SO ₄ CONTAINING VARIOUS CONCENTRATION OF PDTT									
	Conc. of	Tafel data					Impedance data		
	PDTT (mM)	E _{corr} (mV	i _{corr} (mA	βa (mV	βc (mV	E %	Rct	Cdl	η (%)
		vs. SCE)	cm ⁻²)	dec ⁻¹)	dec ⁻¹)		$(\Omega \text{ cm}^2)$	(μF cm ⁻²)	
Blank	0.000	- 433.5	1.6450	68.5	-73.3	_	1.690	2356.47	_
	0.025	- 457.0	0.8054	29.2	-40.9	51.04	1.448	1337.00	43.30
	0.050	-458.1	0.2620	31.0	-35.3	84.10	1.886	1176.00	50.10
	0.076	-451.9	0.1483	107.3	-99.6	91.03	16.000	391.32	83.39

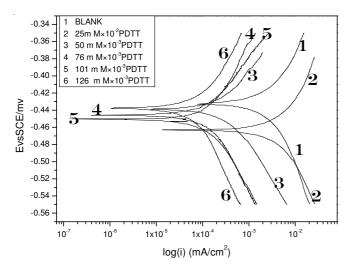
-95.6

-90.3

77.0

62.4

TABLE-1 CORROSION PARAMETERS OBTAINED FROM ELECTROCHEMICAL AND IMPEDANCE MEASUREMENTS FOR MILD STEEL IN 20 % H-SO. CONTAINING VARIOUS CONCENTRATION OF PDTT



-447.2

-438.8

0.1272

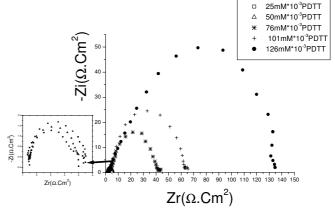
0.0551

Fig. 2. Typical potentiodynamic polarization curves for mild steel in 20 % H₂SO₄ containing different concentrations of PDTT at 25 $^{\circ}$ C

may result from the presence of a pair of electron on sulfur atoms which can absorb strongly on the metal surface³² and also the presence of aromacity of the phenyl and the electron density at this donor group in your oppositions a single pair of electrons on sulfur atoms. The shtifting of $E_{\rm corr}$ indicates that the corrosion inhibitor is an cathodic inhibitor.

Impedance measurement of the mild steel electrode at its open circiut potentiel after 1 h of immersion in 20 % H_2SO_4 solution with and without PDTT inhibitor were performed over the frequency range from 10^5 Hz to 10^{-3} Hz. Fig. 3 shows the obtained Nyquist plots of mild steel in 20 % H_2SO_4 solution in absence and presence of different concentration of PDTT These curves show a typical set of Nyquist plots. It is clear from these plots that the impedance response of carbon steel has significantly changed after addition of the synthesized inhibitors in the corrosive media. This indicates that the impedance of an inhibited substrate increases with increasing concentration of inhibitor in 20 % H_2SO_4 .

The impedance parameters, solution resistance, charge transfer resistance Rct and double-layer capacitance ($C_{\rm dl}$), are listed in Table-1. The Nyquist plots obtained in the real system represent a general behaviour where the double layer on the interface of metal/solution does not behave as a real capacitor. On the metal side electrons control the charge distribution whereas on the solution side it is controlled by ions. As ions are much larger than electrons, the equivalent ions to the charge on the metal will occupy quite a largevolume on the solution side of the double layer²² (Table-1).



24.540

48.740

259.56

51.62

88.98

97.81

BLANK

Fig. 3. Nyquiste plots of mild steel recorded in 20 % H₂SO₄ containing different concentrations of PDTT at 25 °C

$$\eta = \frac{R_{t}^{-1} - R_{t(inh)}^{-1}}{R_{t}^{-1}} \times 100$$
 (2)

The double-layer capacitance (C_{dl}) was calculated from the following equations²³:

$$f(-Z''_{max}) = \frac{1}{2\pi C_{dl}R_{t}}$$
 (3)

where f(-Zimg) is the frequency at maximum imaginary component of the impedance and Rct are the charge transfer resistances.

Where Rt(inh) and Rt are the charge transfer resistance values with and without inhibitor for mild steel in acidic media respectively²⁶. The impedance parameters derived from thes investigation are given in Table-1.

As the PDTT concentration increased, Rt values increased, but C_{dl} values tended to decrease Table-1. The decrease in C_{dl} values was due to the adsorption of PDTT on the metal surface. The inhibition efficiency η reached 97.81 % in 20 % H_2SO_4 at 126×10^{-3} mM of inhibitor. The inhibition efficiency in 20 % H_2SO_4 was lower. This was presumably caused by the lower surface coverage of the inhibitor on the mild steel surface in the 20 % H_2SO_4 solution.

It is clear that charge transfer resistance Rct values were increased and the capacitance values C_{dl} decreased with increasing inhibitors concentration. Decrease in the capacitance, which can result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, suggests that the inhibitor molecules.

Act by adsorption at the metal/solution interface²². The addition of the synthesized surfactants provides lower C_{dl}

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values, probably as a consequence of replacement of water molecules by the synthesized inhibitors at the electrode surface. The inhibitor molecules may also reduce the capacitance by increasing the double layer thickness according to the Helmholtz model²².

The value of C_{dl} is always smaller in the presence of the inhibitor than in its absence, as a result of the effective adsorption of the synthesized inhibitors.

Results obtained from EIS measurements are in good agreement. The real part (Z') and imaginary part (Z") of the cell impedance were measured in ohms at various frequencies.

With that obtained from potentiodynamic polarization Electrochemical impedance spectroscopy and polarization curves measurements were repeated several times and observed that they were highly reproducible.

Inhibition mechanism, the primary step in action of inhibition in acid solution is generally agreed to be adsorption on to the metal surface, wich is usually oxide free in acid solution. The adsorption of inhibitor species (Inh) on the metal surface in aqueous solution should be considered aplace exchanger reaction:

$$Inh_{aq} + xH_2O_{ads} = Inh_{ads} + xH_2O_{aq}$$
 (4)

where x the size ratio is the number of water molecules displaced by one molecule of organic inhibitor. When the equilibrium of the process described in eqn. 4 is reached, it is possible to obtain different expression of the adsoption isotherm plots and thus the degree of surface coverage $\theta = E \%/100$. Can be plotted as a functin of the inhibitor under test³³.

It is well recognized that the first step in inhibition of metallic corrosion is the adsorption of organic inhibitor molecules at the metal/solution interface and that the adsorption depends on the molecule's chemical composition, the temperature and the electrochemical potential at the metal/solution interface. In fact, the solvent $\rm H_2O$ molecules could also adsorb at metal/solution interface so the adsorption of organic inhibitor molecules from the aqueous solution can be regarded as a quasi-substitution process between the organic compounds in the aqueous phase $\rm [Org_{(aq)}]$ and water molecules at the electrode surface $\rm [H_2O_{(ads)}]^{35}$.

$$Org_{(aq)} + xH_2O_{ads} \longrightarrow Org_{(ads)} + xH_2O_{(aq)}$$
 (5)

where x is the size ratio, i.e., the number of water molecules replaced by one organic inhibitor. Basic information on the interaction between the inhibitor and the mild steel surface. It is well recognized that organic inhibitor molecules set up their inhibition action via the adsorption of the inhibitor molecules onto the metal/solution interface. The adsorption process is affected by the chemical structures of the inhibitors, the nature and charged surface of the metal and the distribution of charge over the whole inhibitor molecule. In general, owing to the complex nature of adsorption and inhibition of a given inhibitor, it is not possible for single adsorption mode between inhibitor and metal surface. Organic inhibitor molecules may be adsorbed on the metal surface in one or more of the following ways: (a) Electrostatic interaction between the charged molecules and the charged metal; (b) Interaction of unshared electron pairs in the molecule with the metal and (c) Interaction of π electrons with the metal.

The inhibition efficiency afforded by 4-phenyl-1,2-dithiol-3-thione may be attributed to the presence of electron rich sulfur and aromatic rings³⁵.

Langmuir isotherm for monolayer chemisorptions is given by the following equation³⁴:

$$C_{inb}/\theta = 1/K_{ads} + C_{inb}$$
 (6)

where K_{ads} is the equilibrium constant of the adsorption/desorption process. The plots of C_{inb}/θ . C_{inh} yield straight line with nearly unit slope showing that the adsorption of PDTT can be fitted to Langmuir adsorption as presented in Fig. 4. Adsorption equilibrium constant (K_{ads}) and free energy of adsorption (ΔG°_{ad}) were calculated using the relation ships³⁴:

$$K_{ads} = 1/C_{inb} \times [\theta/(1-\theta)]$$
 (7)

$$\Delta G^{o}_{ad} = 2.3RT \log (55.5 K_{ads})$$
 (8)

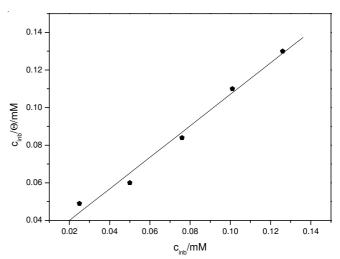


Fig. 4. Langmuir's isotherm plots for the adsorption of PDTT and on the surface of mild steel in 20 % H₂SO₄

The value of 55.5 is the molar concentration of water in solution the values of adsorption equilibrium constant (K_{ads}) and free energy of adsorption (ΔG^o_{ad}).

The negative values of ΔG^{o}_{ad} indicate spontaneity of the adsorption process and stability of the adsorbed layer on the metal surface. Literature reveals that with regard to energetic of the adsorption process: two types of adsorption process had been established, physisorption (electrostatic interaction between the charged molecules and charge metal) in which the ΔG^{o}_{ad} , is up to -20 kJ mol $^{-1}$ and chemisoption (charge sharing or transfer from the inhibitor (adsorbate) molecules to the metal surface to form co-ordinate bond) where the ΔG^{o}_{ad} is more negative than -40 kJ mol $^{-1}$.

The calculated standard free energy of adsorption ΔG^{o}_{ad} in the case of PDTT is -37.38 kJ mol⁻¹ therefore, lower than -20 KJ mol⁻¹. This indicates that the adsorption mechanism is neither typical physisorption nor typical chemisorption, but it is complex mixed type that is the adsorption of the investigated 4-phenyl-1,2-dithiol-3-thione (PDTT) on the mild steel surface in 20 % H_2SO_4 involves both physisorption and chemisorption but chemisorption is predominant mode of adsorption³⁵.

Conclusion

The studied 4-phenyl-1,2-dithiol-3-thione (PDTT) cation shows remarkable inhibition properties for the corrosion of mild steel in 20 % H₂SO₄ at 25 °C and the inhibition efficiency increases with increasing of the PDTT concentration. The inhibitor efficiencies determined by weight loss, Tafel polarization and EIS methods are in reasonable agreement. Based on the polarization results, the investigated (PDTT) can be classified as cathodic inhibitor. The EIS spectra are well described by a relatively simple structural model having only one time constant. The calculated structural parametres show increase of the obtained Rct values and decrease of the capacitance, C_{dl}, with PDTT concentration increase. It is suggested to attribute this to the increase of the thickness of the adsoption layer a tsteel surface. The adsorption model obeys to the Langmuir adsorption isotherm and the negative value of the Gibbs free energy of adsorption (ΔG^{o}_{ad}) indicates that the adsorption of the PDTT is a spontaneous process. High negative value suggests that the inhibitive effect of 4-phenyl-1,2-dithiol-3-thione (PDTT) is due to the formation of a chemisorbed film on the metallic surface and can be used as an excellent corrosion inhibitor for steel in acidic medium at room temperature.

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