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Experimental and Theoretical Investigations of Lansoprazole As Inhibitor for Mild Steel Corrosion in 1M Hydrochloric Acid

KEYWORDS: Lansoprazole drug; inhibition; steel; hydrochloric acid; electrochemical studies; theoretical calculation

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ABSTRACT *The inhibition effect of lansoprazole drug (LP) as an inhibitor on the corrosion of mild steel (MS) in 1M HCl has been studied by electrochemical impedance spectroscopy (EIS) and Tafel polarization. Morphology of the MS specimens was examined using scanning electron microscopy (SEM) in presence and absence of inhibitor. The results show that LP is a good inhibitor and the inhibition efficiency (IE %) increases with the inhibitor concentration. Polarization curves show that LP is a mixed type inhibitor in hydrochloric acid solution. Quantum chemical calculations were performed using the density functional theory to find out whether a clear link exists between the inhibitive effect of the inhibitor and the electronic properties of its main constituents. The results obtained from the Tafel polarizations and EIS are in good agreement with theoretical calculation.*

1. Introduction:

Hydrochloric acid is widely used in various technological processes in industry, e.g., in pickling baths, in the extraction and processing of oil and gas and in other chemical and petrochemical industries. Also, in the technical cracking of petroleum, acids appear as a result of hydrolysis of salts and may have destructive effect on the equipment. Corrosion in mild steels are important and expensive problem in the industries and it represents a significant portion of loss as a result of lost production, inefficient operation, high maintenance. The use of corrosion inhibitors has become an answer to the corrosion attack of metals. Inhibitors should be effective in low concentrations for economy. The search for efficient inhibitors for MS corrosion is ongoing globally. Due to their cost effectiveness, a lot of research effort is now geared at inhibiting the corrosion of MS in acidic medium using organic compounds (1-3). Organic inhibitors reduce the rate of corrosion of a metal/alloy by adsorbing on its surface, thereby blocking its active corroding sites. In literature, several authors have paid attention on the development of drugs as inhibitors for metallic corrosion (4-6). The drugs are reportedly environmentally friendly and important in biological reactions and it can be easily produced and purified. The present study investigates the inhibitive effect of lansoprazole (IUPAC name: 2-(((3-methyl-4-(2,2,2-trifluoroethoxy)pyridin-2-yl)methyl) sulfinyl)-1H-benzo[d]imidazole) on the corrosion of MS in 1M HCl solution by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) methods.

2. Materials and methods:

The inhibitor compound was purchased as lansoprazole (trade name – LAN-15) from pharmaceutical store, manufactured by INTAS pharmaceuticals, Dehradun (India). Stock solution of LP was prepared by recrystallisation with ethanol and it is used for all experimental purposes. Molecular structure of the LP is presented in figure 1. The working electrode was polished with different grades of emery papers (1/0 to 6/0), washed with water and degreased with acetone. All electrochemical measurements were carried out using a CHI 760D electrochemical impedance analyzer model. Prior to the measurement, a stabilization period of 30 minutes was allowed, which was proved to be sufficient to attain a stable value of open circuit potential (OCP).. These studies were made using a three-electrode cell assembly and the working electrode was MS with the exposed surface of 1cm^2 and the rest being covered by using commercially available resin. The measurements were carried out by using ac signal of 0.1V amplitude for the frequency spectrum from 100 kHz to 0.01Hz in the potential range of + 200 mV. In the EIS measurements the R_{ct} values were used to calculate the IE %, according to the following expression [7];

$$IE\ (\%) = \left[\frac{R_{ct}^{i} - R_{ct}^{o}}{R_{ct}^{i}}\right] \times 100 \qquad (1)$$

where,
I_{corr}^{o} and I_{corr}^{i}
are the charge transfer resistance values with and without LP, respectively, and the IE % values were calculated from the Tafel polarization is as follows;

$$\mathbf{E}\ (\%) = \left[\frac{I_{corr}^{o} - I_{corr}^{i}}{I_{corr}^{o}}\right] \times 100 \qquad (2)$$

where, I_{corr}^{o} and I_{corr}^{i} are the corrosion current densities in the absence and presence of LP, respectively. All geometry optimizations and quantum chemical calculations were performed using density functional theory (DFT) and utilizing the 3-21 G (d,p) basis set. DFT/B3LYP is recommended for the study of chemical reactivity and selectivity in terms of the frontier molecular orbital [8]. The scanning electron microscopy VEGA3TESCAN model was used to study the morphology of corroded surface in the presence and absence of LP. The specimen, after dipping for 3 hours at the room temperature, was thoroughly washed with doubly distilled water before putting on the slide.

3. Results and Discussion

3.1. Electrochemical impedance spectroscopy

Table 1 shows the experimental results obtained from EIS measurements for the corrosion of MS in the presence of LP at room temperature. The impedance spectra for MS in 1M HCl solution without and with optimum concentration of LP are presented as Nyquist plot in figure 2. Clearly, the plot exhibits a large capacitive loop at high frequencies followed by a small inductive loop at low frequency values. The capacitive loop indicates that the corrosion of steel is mainly controlled by a charge transfer process, and usually related

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to the charge transfer of the corrosion process and double layer behavior. On the other hand, the inductive loop may be attributed to the relaxation process obtained by adsorption of inhibitor on the electrode surface [9]. The interfacial double layer capacitance (C_{dl}) values have been estimated from the impedance value using Nyquist plot by the formula (3):

$$C_{dl} = (2\pi f_{\max} R_{ct})^{-1} \quad (3)$$

The double layer between the charged metal surface and the solution is considered as an electrical capacitor. The adsorption of inhibitor on the electrode surface (MS) may be attributed to the formation of a protective layer on the surface. The thickness of this protective layer δ_{inh} was related to C_{dl} by the following equation [10];

$$\delta_{inh} = \frac{\varepsilon_0 \varepsilon_r}{C_{dl}} \quad (4)$$

where, ε_0 is the dielectric constant and ε_r is the relative dielectric constant. By increasing the LP concentrations from 50 to 300 ppm, the Rct values increase but C_{dl} values decrease. The decrease in the C_{dl} value is due to the adsorption of the inhibitor on the steel surface. The adsorption of the LP on MS surface can occur either directly on the basis of donor– acceptor interaction between the π-electrons (of the double bonds) and the vacant d orbital of steel surface atoms or interaction of them with already adsorbed chloride ions as proposed [11-12]. Adsorption might also occur in the cationic form with positively charged part of the molecule oriented toward negatively charged MS surface. The simplest fitting is represented by Rundles electrical equivalent circuits used to fit the experimental results as previously reported [13]. The table 1 confirms that the IE % increases with the concentrations of LP and maximum efficiency (88.95 %) reaches at 300 ppm of LP. All the above results infer that with increase in LP concentration, the productive film is more and more protective.

3.2. Tafel polarization

Polarization measurements have been carried out in order to gain knowledge concerning the kinetics of the anodic and cathodic reactions. The corrosion current density (I_{corr}) and corrosion potential (E_{corr}) are obtained by the extrapolating the anodic and cathodic current–potential curves (Figure 3). Table 2 shows the electrochemical parameters (I_{corr}, E_{corr}, ba and bc) obtained from Tafel plots for the MS electrode in 1M HCl solution without and with different concentrations of LP. Under the experimental conditions performed, the cathodic branch represents the hydrogen evolution reaction, while the anodic branch represents the iron dissolution reaction. It can be seen that the cathodic (bc) and anodic Tafel slopes (ba) remain almost unchanged with increasing inhibitor concentration. It is clear that the studied LP compound act as a corrosion inhibitor suppressing both anodic and cathodic reaction by getting adsorbed on the MS surface by simply blocking the active sites [14], and these results suggested that the addition of LP reduces the anodic dissolution and also retards the cathodic hydrogen evolution reaction. Also, the E_{corr} shifts have no definite trend which indicates that this molecule act as mixed type inhibitor. From table 2, it is clear that the corrosion current density (I_{corr}) values decreases from 1.180 $mAcm^{-2}$ to 0.1327 $mAcm^{-2}$ with the addition of various concentration of LP. When the I_{corr} decreases the IE % increases from 50.75 to 88.75%. It is also found that R_p value increases with increasing inhibitor concentration, which suggests the retardation of MS corrosion in inhibited solution compared to uninhibited.

The inhibition efficiency calculated from the electrochemical impedance spectroscopy (88.95 %) is correlated with IE % obtained by Tafel polarization (88.75 %).

3.3. Theoretical calculation

Quantum chemical studies have been successfully implemented to correlate the corrosion protection efficiency of organic inhibitors with their calculated molecular orbital (MO) energy levels. The chemical reactivity of molecules is often discussed in term of quantum chemical parameters such as the Highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO), and electron density parameters such as the dipole moment (μ) and mulliken charges. The energy of the HOMO (E_{HOMO}) represents the ability of the molecule to donate a lone pair of electrons and the higher the E_{HOMO} value, the greater the tendency of the molecule to donate electrons to an electrophilic reagent [15] and the lower the E_{LUMO} is, the greater the tendency of the molecule to accept electrons from metal atoms. Results from table 3 show that LP has low E_{LUMO} and high E_{HOMO} values compared with many organic compounds. The energy difference between E_{HOMO} and E_{LUMO} (i.e., ΔE) informs of the reactivity of the given compound; the smaller the ΔE value, the greater the reactivity of the molecule. The results show that LP has the smallest ΔE value (0.17412) and is therefore the most reactive molecule. The dipole moment gives information on the polarity. The higher the dipole moment, the higher is the polarity of the molecule. In the study of corrosion inhibition, the IE % has been reported to increase with increase in the dipole moment of the inhibitor [16]. The HOMO and LUMO diagrams (Figure 4 b-c) of the LP, reflect that the orbital electron densities were distributed homogeneously throughout the molecules. Therefore the more negative Mulliken atomic charges of the adsorbed inhibitor, the more easily the atom donates its electrons to the unoccupied orbital of the metal and adsorb preferentially on the metal surface with the formation of a closely packed adsorption layer to inhibit iron ions from entering the solution. It is clear from figure 4a that nitrogen and oxygen atoms carrying negative charges could offer electrons to the metal surface to form a coordinate type bond.

3.4. Scanning electron microscopy

The micrographs showed properties of the MS surface after immersion in 1.0 M HCl in the absence and the presence of 300 ppm of LP at 30°C. The micrographs revealed that the steel surface in presence of LP (figure 5 a) improved while the steel surface immersed in HCl solution (figure 5 b) was rough and covered with corrosion products. There are less pits and cracks observed in the inhibited surface. The MS surfaces are fully covered with the LP molecules and a protective film was formed.

3.5. Mechanism of Corrosion Inhibition

The IE % of the given inhibitor against the corrosion of MS in 1M HCl can be explained on the basis of the number of adsorption sites, their charge density, molecular size, mode of interaction with the metal surface and the ability to form metallic complex. We can note that a possible mechanism of corrosion inhibition of steel in 1M HCl by the compound under study may be deduced on the basis of adsorption. In addition to the chemical adsorption, the inhibitor molecules can also be adsorbed on the steel surface via electrostatic interaction between the charged metal surface and the charged inhibitor molecule if it is possible. Analysis of the electrochemical data showed that the inhibiting properties increased with an increase in the concentrations of LP. It is due to presence of more number of electron donating groups in the LP molecule. Therefore, based on our experimental and theoretical findings, firstly the chloride ions of hydrochloric acid get adsorbed on the MS surface [18], and in steps led to the formation of ferrous ions. Thereafter, the inhibitor gets attracted towards MS and interacts coordinatively with ferrous ion, followed by adsorption on the MS surface to protect the corrosion.

4. Conclusions:

On the basis of the above results the following conclusion can be drawn.

- The polarization curves inferred that the LP drug acting as mixed type inhibitor. The results also demonstrate that the inhibition was attributed to the adsorption of the inhibitor on the MS surface.

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- On the other hand, the values of C_{dl} have showed a tendency to decrease, which could be resulting from a decrease in local dielectric constant and/or an increase in thickness of the LP through adsorption at the metal/solution interface.
- The calculated quantum chemical properties such as dipole movement, Mulliken charges, highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbital energies at B3LYP/3-21G (d,p) level also give evidences that the molecule, LP, showed higher corrosion protection efficiency. This corroborates well with our experimental finding.
- The SEM images confirm the formation of protective layer on the MS surface.

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Table 1. Electrochemical impedance parameters for MS in 1 M HCl containing various concentrations of LP.

Concentration of Inhibitor (ppm)	f_{max} (Ωcm^2)	R_{Ct} (Ωcm^2)	C_{dl} ($\mu F\ cm^{-2}$)	I.E η (%)
Blank	6.651	12.874	185.8	-
50	22.624	43.574	161.39	70.45
100	41.527	81.942	46.753	84.29
150	47.342	93.252	36.036	86.19
200	49.835	97.266	32.821	86.78
250	57.868	114.09	24.097	88.72
300	60.019	116.52	22.748	88.95

Table 2. Tafel polarization values for the corrosion of MS in 1 M HCl in the absence and presence of various concentrations of LP.

Concentration of Inhibitor (ppm)	bc (V/dec)	ba (V/dec)	E_{corr} (mV/SCE)	I_{corr} (mA/cm2)	Linear polarization (Ohm)	I.E. (%)
Blank	6.191	7.632	-469.5	1.180	27	-
50	7.577	7.859	-496.3	0.5811	49	50.75
100	8.521	9.702	-526	0.426	56	63.89
150	7.046	10.10	-475.6	0.2805	90	76.23
200	6.664	10.00	-476.4	0.2279	115	80.69
250	6.515	8.69	496.5	0.1829	156	84.50
300	8.066	8.87	478.2	0.1327	193	88.75

Table 3: Quantum chemical parameters of LP

E_{HOMO} (eV)	E_{LUMO} (eV)	μ (D)	ΔE	E	I.E (%)*
-0.22582	-0.0517	2.3827	0.17412	-1621.75	88.95

*I.E (%) values were calculated from EIS measurement.

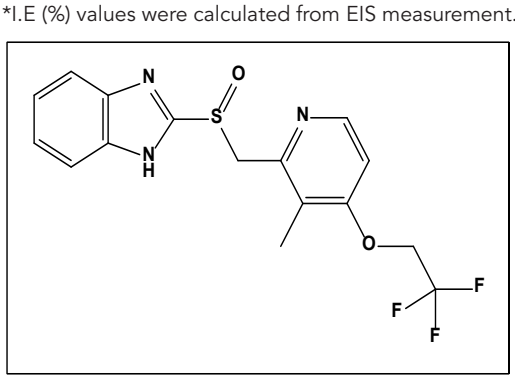


Figure 1: Structure of lansoprazole (IUPAC name: 2-(((3-methyl-4-(2,2,2-trifluoroethoxy)pyridin-2-yl)methyl) sulfinyl)-1H-benzo[d]imidazole)

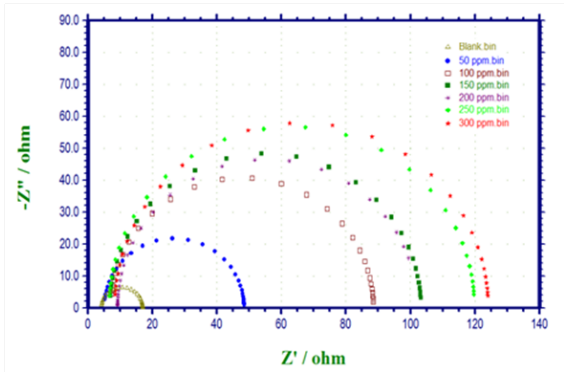


Figure 2: Nyquist plots of MS in 1 M HCl solutions with various concentrations of LP drug.

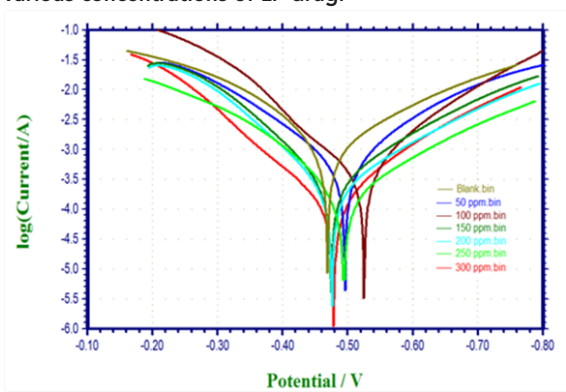
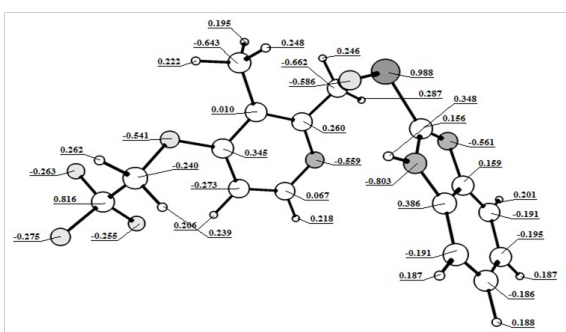
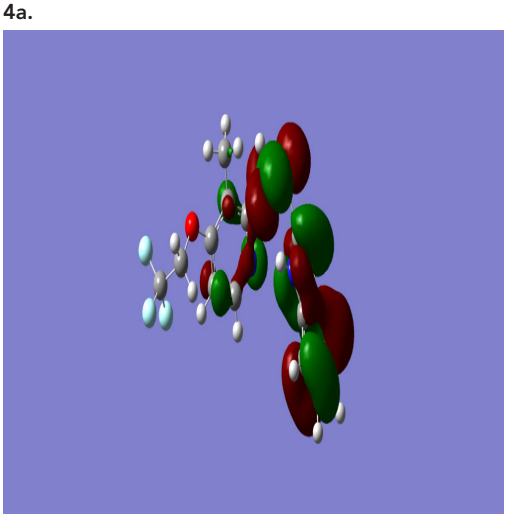


Figure 3: Tafel polarization plots of MS in 1 M HCl solutions with various concentrations of LP drug.



4a.



4b

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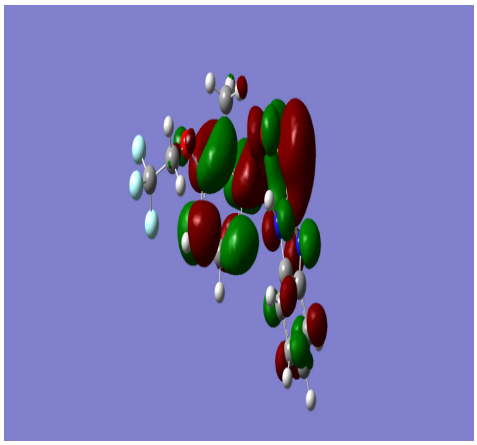
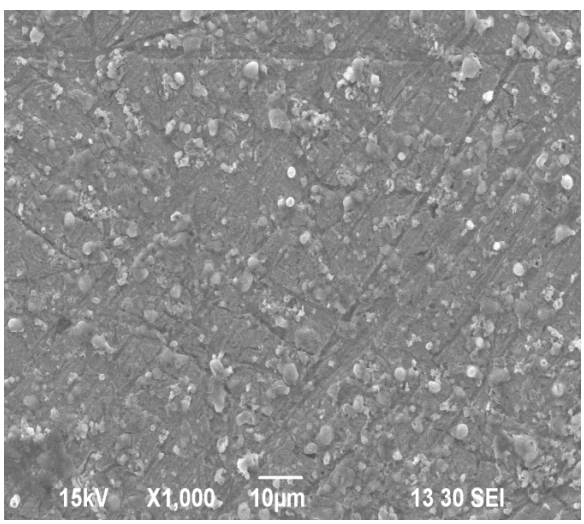
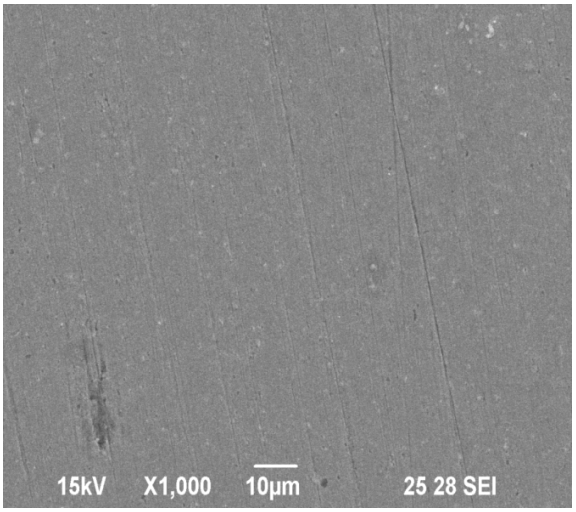


4c
Figure 4: (a) Mulliken charge distribution (c) HOMO Structure (d) LUMO structure



5a



5b
Figure 5: SEM images of MS (a) 1 M HCl solution (b) 1 M HCl solutions with optimum concentration of LP (300 ppm).

REFERENCE

1. Abd El Rehim, S.A.; Hassan, H.H.; Amin, M.A. Corros. Sci. 2004, 46, 5. | 2. Fouda, A.S.; Gouda, M.M.; El- Rahman, S.I. Chem. Pharm. Bull. 2000, 48, 636. | 3. Ebenso, E.E. Part 1. Bull. Electrochem. 2003, 19, 209. | 4. Obot, I.B.; Obi-Egbedi, N.O.; Umoren, S.A. Corros. Sci. 2009, 1868. | 5. Shukla, S.K.; Quraishi, M.A. Corros. Sci. 2009, 51, 1007. | 6. Omar, A.; Hazazi; Abdallah, M. Int. J. Electrochem. Sci. 2013, 8, 8138. | 7. karthik, G.; Sundaravadivelu, M. ISRN Electrochem. 2013. http://dx.doi.org/10.1155/ 2013/403542. | 8. Senet, P. Chem. Phys. Lett. 1997, 275, 527. | 9. Bentiss, F.; Traisnel, M.; Lagrenee, M. Corros. Sci. 2000, 42, 127. | 10. Hassan, H.H. Electrochim. Acta 2006, 51, 5966. | 11. Murakawa, T.; Nagaura, S.; Hackerman, N. Corros. Sci.1967, 7, 79. | 12. Goncalves, R.S.; Azambuja, D.S.; SerpaLucho, A.M. Corros. Sci. 2002. 44, 467. | 13. Karthik, G.; Sundaravadivelu, M.; Rajkumar, P. Res. Chem. Intermed. 2013, doi: 10.1007/s11164-013-1291-0. | 14. Mistry, B.M.; Patel, N.S.; Sahoo, S.; Jauhari, S. Bull. Mater. Sci. 2012, 35(3), 459. | 15. Fedorov, A.; Zhuravlev, Y. N.; Berveno, V. P.; Phys. Chem. Chem. Phys. 2011, 13, 5679. | 16. Eddy, N.O.; Awe, F.E.; Gimba, C.E.; Ibisi, N.O.; Ebenso, E. E. Int. J. Electrochem. Sci. 2011, 6, 931. | 17. Abd El-Makoud, Appl. Surf. Sci. 2003, 206, 129