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Synergistic effect between Starch and Substituted Piperidin-4-one on the Corrosion Inhibition of Mild Steel in Acidic Medium

Brindha.T[a], Mallika. J[a]*, Sathyanarayana Moorthy.V[b]
[a]Department of Chemistry, [b]Department of Physics, PSG College of arts and science, Coimbatore, TamilNadu, India- 641 014.

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**Corresponding Author. E-mail: jmpsgcas@gmail.com; Tel: +91 9600985123.*

Abstract

The corrosion inhibition of mild steel in 1 N Hydrochloric acid in presence of natural polysaccharide (starch) is studied using Electrochemical Impedance Spectroscopy (EIS), potentiodynamic polarization and weight loss measurements. The effect of addition of very small concentration (0.2mM) of 2,6-diphenyl-3-methylpiperidin-4-one (DPMP) on the corrosion behaviour of starch is studied. The temperature effect (30- 55° C) and the time effect (1, 2, 3, 4 and 24 h) are studied for starch, DPMP, individually and for the mixture of starch and DPMP. The effect of DPMP on the corrosion behaviour of starch appears to be synergistic in nature. The mixture of starch and DPMP shows greater stability towards higher temperature and immersion period of 24 h. The formation of protective layer on mild steel surface is confirmed by FT-IR spectroscopy. The quantum chemical parameters such as highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) and band energy gap (ΔE) are calculated as a supportive evidence.

Key words: Corrosion inhibition, Synergism, 2,6-diphenyl-3-methylpiperidin-4-one, EIS, quantum chemical studies.

1. Introduction

Corrosion is one of the greatest industrial problems nowadays, causing several material and financial losses. To ease the problem, corrosion inhibitors have been used. However, the high toxicity of the inhibitors helped the development of new kind of inhibitors, harmless to the environment. Most of the effective inhibitors used contain heteroatom such as O, N, S and multiple bonds in their molecules through which they are adsorbed on the metal surface. It has been observed that adsorption depends mainly on certain physio-chemical properties of the inhibitor group, such as functional groups, electron density at the donor atom, π-orbital character, and the electronic structure of the molecule. The use of chemical inhibitors has been limited because of the environmental threat, recently, due to environmental regulations.

Several researchers investigated the corrosion inhibition efficiency of large number of polymers for mild steel [1-13], aluminium [14-20], copper [21-23] and other metals [24, 25]. However most of the polymers have limited application due to their low solubility in acidic solutions. Several researches have indicated that some polymers can be used as corrosion inhibitors because, through their functional groups, they form complexes with metal ions on metal surfaces. These complexes occupy a large surface area, thereby blanketing the surface and protecting the metals from corrosive agents present in the solution. The corrosion inhibition of polymethacrylic acid and styrene maleic acid co-polymer on zinc pigments in aqueous alkaline medium was studied by Muller et al, [26]. The combination of Carboxy methyl cellulose and Zn^{2+}on the corrosion inhibition of carbon steel in NaCl solutions produces strong inhibition potential [27]. In the present study, the synergistic effect between starch and 2,6-diphenyl-3-methylpiperidin-4-one have been investigated. More recently, Mobin et al, [28] investigated starch in combination with surfactants as corrosion inhibitors for mild steel in acid medium. And modified cassava starches were evaluated as corrosion inhibitor for carbon steel under alkaline conditions [29]. Many heterocyclic compounds have been used as corrosion inhibitors either alone or with other compounds to improve their efficiency towards corrosion. Combination of inhibitors provides enhanced effects due to synergism are reported in various literatures [30-32].

2. Materials and Methods

2.1. Chemicals used

All the reagents used in this experiment ethanol, benzaldehyde, ketones, ammonium acetate, starch were of analytical grade and were used without any further purification. Acid used for the study were also of Analar grade and double distilled water was used for the dilution.

2.2. Synthesis of substituted piperidin-4-one

2,6-diphenyl-3-methylpiperidin-4-one (DPMP) were synthesized via procedure was that of Noller and *Baliah* [33] . Dry ammonium acetate (0.05 mol) in glacial acetic acid (0.1 mol), benzaldehyde (0.15 mol) and butanone (0.15 mol) were added together and allowed to stand for several hours. Then the solid mass obtained was washed with ethanol: ether mixture. Crystallisation of the product from ethanol gave 2, 6-diphenyl-3 methylpiperidin-4-one (m.p.96^{o}C).

2.3. Mild steel specimens

Mild steel specimens of the following composition have been used all over the present investigations (Carbon: 0.07 %, Sulphur: Nil, Phosphorous: 0.008%, Manganese: 0.34%, remaining ferrous).

2.4. Methods

In the gravimetric experiment, mild steel specimen of the dimensions 2.5 cm × 1 cm × 0.1 cm has been used. It was polished using 1/0, 2/0, 3/0, and 4/0 emery papers, washed with double distilled water, dried and finally degreased with the acetone. In this method previously weighed coupon was completely immersed in 100 ml 1 N hydrochloric acid with and without inhibitor in an open beaker. After an hour, the corrosion product was removed by washing each coupon using double distilled water. The washed coupon was rinsed in acetone and dried in the air before reweighing. From the average weight loss (mean of three replicate analysis) results, the inhibition efficiency (IE %) of the inhibitor, and the corrosion rate of mild steel (CR) were calculated using the following equations:

Corrosion rate (mmpy) = (870.6 x W) / (D x A x T)
Where, W = weight loss in mg,
D = density in mg,
A = area of exposure in cm^2 and
T = time in hours.

Inhibitor efficiency has been determined by using the following relationship.

I.E (%) = $W_o – W_{t\,/}\, W_o$

W_o= Weight loss without inhibitor, Wt = the weight loss with inhibitor.

The effect of temperature on the corrosion inhibition performance for the mixture of starch and DPMP was studied in the range of 30 - 55^{o}C. Also, to study the effect of immersion time for this mixture on the corrosion inhibition behaviour was studied at various immersion periods [1,2,3,4 and 24 h].

Two electrochemical techniques were employed to observe the corrosion process for both inhibited and uninhibited media. These were electrochemical impedance spectroscopy and potentiodynamic polarization techniques. The electro chemical impedance measurements were carried out over the frequency range of 10 KHz to 0.01 Hz carried with AC signed amplitude of the 10 mV at the corrosion potential. The measurements were automatically controlled by Z_{view} software and the impedance diagrams are given as Nyquist plots. From the plots the electrochemical parameters such as double layer capacitance (C_{dl}) and charge transfer resistance (R_{ct}) calculated. The potentiodynamic polarization measurements were made for a potential range of -200mV to +200 mV with respect to open circuit potential, at a scan rate of 1mV/sec. From the plot of E Vs log I, the corrosion potential (E_{corr}), corrosion current (I_{corr}) were obtained. Tafel slopes b_a and b_c were obtained in the absence and in the presence of inhibitors. From the I_{corr} values the inhibition efficiencies were calculated. The corrosion rate was obtained from the relationship:

Corrosion rate (C_R mmpy) = 3.2 x I_{corr} (mA/cm^2) x $\frac{Eq\ wt}{density}$

and inhibition efficiency:

IE % $= \frac{Icorr\ (o) - Icorr\ (i)}{Icorr\ (o)}$ x 100

Where, $I_{corr(0)}$ is the corrosion current in the absence of inhibitor and $I_{corr(i)}$ is the corrosion current in the presence of inhibitor.

A Shimadzu FT-IR 8000 Spectrophotometer in the 4000-400 cm^{-1} region using the KBr disc technique was employed to examine the interaction of inhibitors with the metal surface. Vibration bands were reported as wave number (cm^{-1}).

3. Results and discussion

3.1. Weight loss measurements

The corrosion of mild steel in 1 N hydrochloric acid in the absence and presence of starch and DPMP are studied using weight loss technique at room temperature. The inhibition efficiencies and corrosion rates for the starch and DPMP at different concentrations are calculated and the results are given in Table 1.

From the Table 1 it is clear that the corrosion rates are reduced in the presence of starch as compared to free acid solution. The inhibition efficiency increases upto 0.4 mM and further increase in concentration does not significantly influence the inhibition efficiency. Analysis of the results of DPMP shows the direct relationship between concentration of the inhibitor and its inhibition efficiency. The corrosion rates are reduced in the presence of DPMP as compared to free acid solution. The inhibition efficiency of starch and DPMP are analysed at higher temperatures and the results are included in Table 1. The temperature studies for both the compounds are showing better inhibition efficiency only at room temperatures.

Table 1: Inhibition efficiencies of starch and DPMP on mild steel in 1 N hydrochloric acid at different temperatures

Conc (mM)	Inhibition efficiency (%)						Corrosion rate(mmpy)					
	Starch			DPMP			Starch			DPMP		
	30^{o}C	45^{o}C	50^{o}C	30^{o}C	45^{o}C	50^{o}C	30^{o}C	45^{o}C	50^{o}C	30^{o}C	45^{o}C	50^{o}C
Blank	---	-----	----	-----	----	----	0.213	0.279	0.328	0.230	0.296	0.493
0.1	35.2	30.3	25.7	22.8	19.6	10	0.128	0.194	0.246	0.177	0.246	0.420
0.2	41.5	35.6	32.1	30.0	26.4	11.2	0.124	0.180	0.249	0.148	0.233	0.394
0.4	46.1	34.5	30.4	45.7	40.1	27.6	0.115	0.162	0.200	0.124	0.171	0.315
0.6	36.9	32.1	27.4	51.4	44.3	39.6	0.134	0.138	0.207	0.118	0.175	0.328
0.8	36.1	29.8	32.3	50.9	41.6	32.3	0.136	0.095	0.230	0.122	0.177	0.325

The stability of these two inhibitors are checked by performing the experiments for various immersion periods. They show better inhibition efficiency only upto 2 h of immersion period.

To improve the efficiency with respect to temperature and immersion time, combinations of starch and DPMP are tried and the results are given in the Table 2.

Analysis of the results in Table 2 shows that the Starch and DPMP in ratio 2:1 give better results. A combination of 0.4 mM starch and 0.2 mM DPMP reduces the corrosion rates drastically and the inhibition efficiency gets almost doubled. So this combination is taken as suitable mixture and its inhibition efficiencies are tested upto 55^{o} C and 24 h of immersion period at room temperature.

Table 2: Synergism parameters and inhibition efficiencies of combination of varying amounts of starch and DPMP on mild steel in 1 N hydrochloric acid

Conc (mM)		Inhibition efficiency (%)	Synergism parameter (S_1)	Degree of surface coverage(Θ)
Starch	DPMP			
0.2	0.2	43.2	1.67	0.432
0.4	0.2	72.4	1.05	0.724
0.6	0.2	65.1	1.28	0.651
0.2	0.4	45.6	1.93	0.456
0.4	0.4	49.3	1.87	0.493
0.6	0.4	59.2	1.40	0.592
0.8	0.4	60.6	1.35	0.606
0.4	0.6	51.2	1.99	0.512
0.6	0.6	51.2	1.73	0.512
0.8	0.6	68.7	1.27	0.687

3.2. Effect of immersion time

The weight loss of mild steel in acidic solution nearly varied linearly with immersion period in the presence of starch and DPMP mixture at room temperature (Figure 1) [34]. It reveals that the inhibition efficiency of 0.4 mM (starch) and 0.2 mM (DPMP) combination gives consistent results for the immersion periods of 1, 2, 3, 4 and 24 hrs.

The protective films formed in the presence of mixture of starch and DPMP after the various immersion periods are visible, which shows that on increasing the time of immersion, a thin film covers the mild surface like a paint coating [35]. These results reveal that the corrosion resistance properties of combined system of starch and DPMP enhances with the immersion period. At the same time, there is no fall in the inhibition efficiency and the surface of the steel looks bright, which showed that the immersion time has no significant effect and also such lower concentration of the combined starch and DPMP is very effective on the corrosion inhibition of mild steel in 1 N hydrochloric acid.

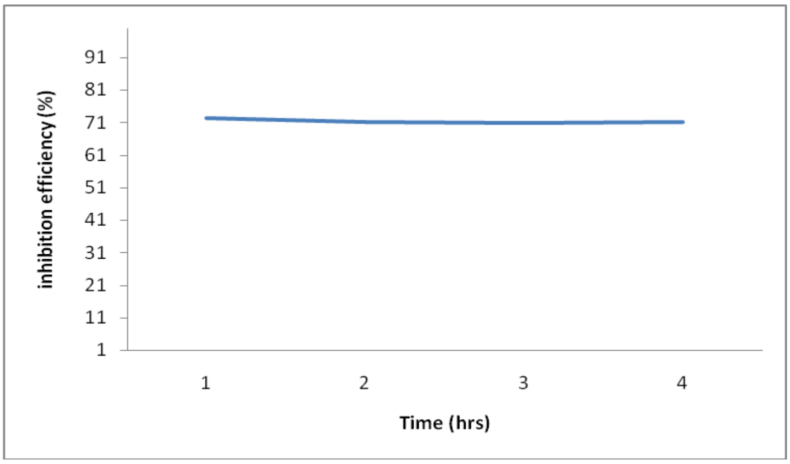


Figure 1: Effect of immersion time on corrosion of mild steel in the presence of starch and DPMP

3.3. Effect of Temperature

The corrosion behaviour of mild steel in acidic medium in the presence and absence of starch in combination with DPMP of optimum concentration is studied in the temperature range of 30- 55° C.

Table 3: Inhibition efficiencies of optimum concentrations of starch and DPMP in 1 N Hydrochloric acid at various temperatures

Concentration	Inhibition efficiency (%)			Energy of activation (E_a)
	30°C	45°C	55°C	kJ/mol
Blank (HCl)	---	---	---	17.07
0.2 mM DPMP	30	26.4	11.2	18.90
0.4 mM (starch)	46.1	34.5	30.4	18.78
0.2 mM DPMP+ 0.4 mM (starch)	72.4	68.0	62.3	19.14

Table 3 reveals that the inhibition efficiency of starch with DPMP at 30° C to 45° C is almost found to be similar. Even at 55° C, the inhibition efficiency lowers to very negligible percentage, indicating their stability at higher temperature.

The activation kinetic analysis is opted for 0.2 mM DPMP, 0.4 mM starch and for the mixture of starch and DPMP. The logarithm of corrosion rate could be represented as a straight line function of 1000/T which is given by the equation:

$$\ln CR = -E_a/RT + \ln A$$

where, Ea = energy of activation, R= universal gas constant, T= absolute temperature and A= pre-exponential factor.

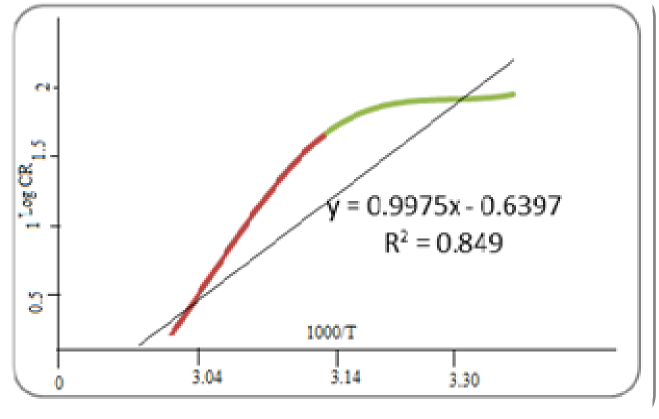


Figure 2: Arrhenius plot for the corrosion inhibition of on mild steel in 1 N Hydrochloric acid

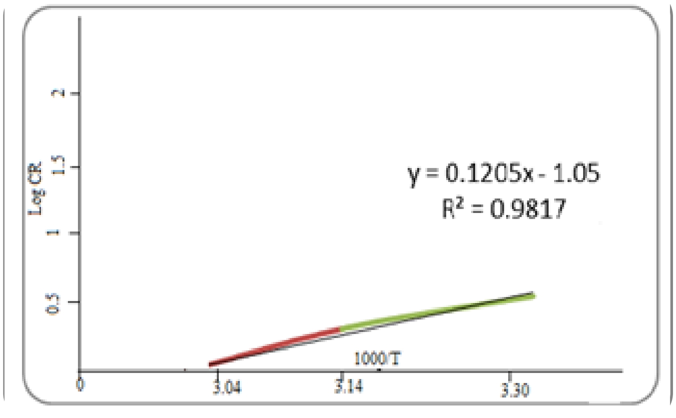


Figure 3: Arrhenius plot for the corrosion inhibition of mild steel in presence of 0.4 mM starch in 1N Hydrochloric acid

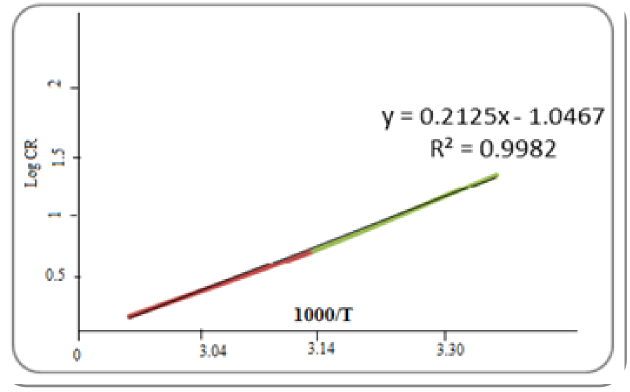


Figure 4: Arrhenius plot for the corrosion inhibition of mild steel in presence of 0.2 mM DPMP in 1N Hydrochloric acid

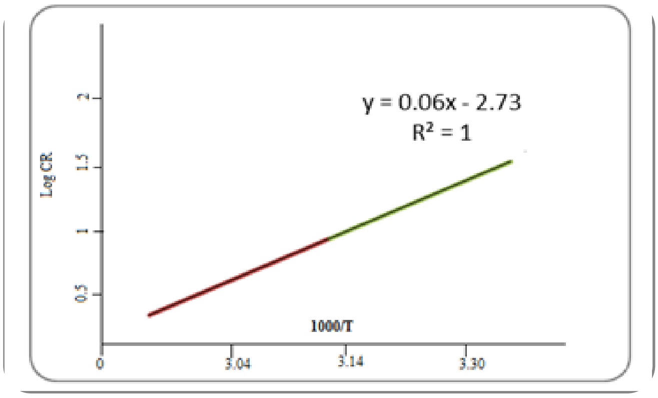


Figure 5: Arrhenius plot for the corrosion inhibition of mild steel in presence of mixture of starch and DPMP in 1N Hydrochloric acid

Arrhenius plots between log CR and 1000/T are given in the Figure [2-5], and the values of activation energy (E_a) are included in the Table 3. Since activation energy is a parameter reflecting the sensitivity change due to the temperature change [36], the mixture of starch and DPMP shows higher activation energy of 19.14 KJ/mol comparing to DPMP (Ea = 18.90 KJ/mol) and starch (Ea = 18.78 KJ/mol) alone.

3.4. Effect of synergism

To observe the existence of synergism between starch and DPMP, the synergistic parameter, S_1 was evaluated using the relationship [37]:

$S_1 = 1 - I_{1+2}/1 - I'_{1+2}$

Where, I_{1+2} ; I_1 is the inhibition efficiency of starch, I_2 is the inhibition efficiency of DPMP and I'_{1+2} is the inhibition efficiency of starch in combination with DPMP.

The S_1 parameters for various concentrations of combination of starch and DPMP are presented in Table 2. The synergism parameter S_1 is found to be greater than unity indicating that the enhanced inhibition efficiency caused by the addition of DPMP is due to synergism.

3.5. Behaviour of inhibitors in the corrosive medium

Starch is biodegradable natural polymer and available in abundant at low cost. The main composition of the starch is polysaccharide carbohydrate consisting of a large number of glucose units joined together by glycosidic bonds. The two important components of starch are amylase (15–20%), and amylopectin (80–85%). Though these two compounds have many conformations, chair form is favoured form. The molecular structure of the starch suggests that it has strong potential to become an effective corrosion inhibitor. But, in acidic medium, starch is hydrolysed into simpler carbohydrates. Due to hydrolysis, the glycosidic linkages in starch are broken to give glucose units. So the inhibition efficiency is mainly due to glucose molecules, which are existing in chair conformation. The existence of glucose molecules is further proved by testing the inhibited solution with Iodine. The colour of the solution remains yellow-red, which indicates the presence of glucose units.

DPMP is also more stable in chair conformation [33]. When starch is added to DPMP containing corrosive medium, the glucose units of starch acts as dispersing agent. The glucose molecules are strongly adsorbed onto the DPMP molecules and give uniform dispersion of the DPMP on the mild steel in corrosive medium.

3.6. Potentiodynamic polarization studies

Potentiodynamic polarization studies were carried out for the corrosion of mild steel in 1 N hydrochloric acid solution in the presence and absence of mixture of inhibitors. The electrochemical parameters E_{corr} (corrosion potential) and I_{corr} (corrosion current density) were obtained by the extrapolation of anodic and cathodic Tafel slopes. Tafel constant b_a and b_c were obtained from anodic and cathodic polarization curves respectively. These parameters are listed in Table 4.

The addition of mixture of starch and DPMP lowers the I_{corr} value significantly and this indicates the inhibiting nature of the inhibitors. The inhibition efficiency and corrosion rates have been calculated and the results are included in Table 4. Also, Figure 6 indicates that the mixture of starch and DPMP behaves as a mixed type of inhibitor.

Table 4: Potentiodynamic polarization parameters for the corrosion inhibition of mild steel in 1N hydrochloric acid with and without inhibitors

Sl.No	Inhibitor Concentration	I_{corr} ($_{mV/cm}{}^2$) x 10^{-4}	E_{corr} ($_{mV/SCE}$)	b_a (mv/dec)	b_c ($_{}$mv/dec)	Corrosion rate (mmpy)	IE (%)
1.	Blank(HCl)	5.46	-0.4720	0.077	0.112	5.890	----
2.	0.4 mM starch	3.85	-0.4989	0.070	0.126	5.464	32.2
3.	0.2 mM DPMP	3.12	-0.4937	0.068	0.129	4.764	44.0
4.	0.4 mM Starch + 0.2 mM DPMP	2.86	-0.4920	0.066	0.123	4.376	50.0

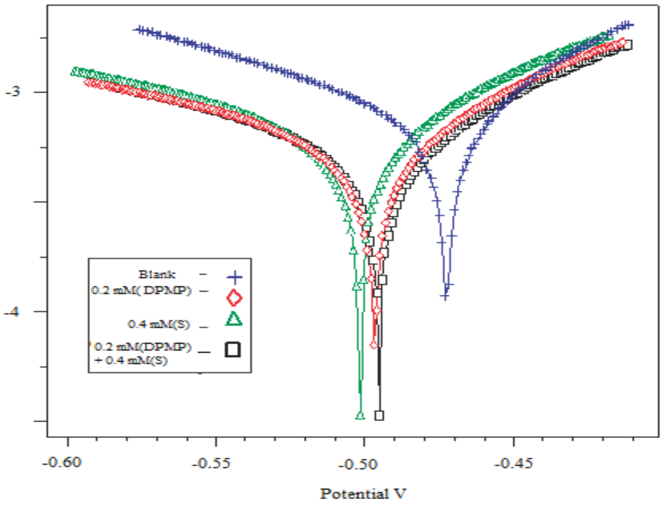


Figure 6: Potentiodynamic polarization for the corrosion inhibition of mild steel in 1N Hydrochloric acid in absence and presence of inhibitors

3.7. *Electrochemical impedance spectroscopic studies*

The corrosion behaviour of mild steel in various acidic solutions in presence of and absence of mixture of inhibitors has been investigated by EIS method at 30^0C. Nyquist plot was recorded and typical plot is given in Figure 7. Impedance parameters like charge transfer resistance (R_t) ,double layer capacitance (C_{dl}) are given in Table 5.

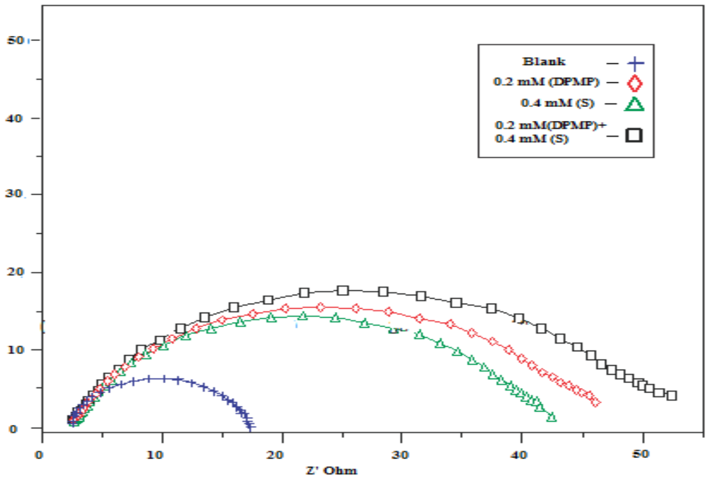


Figure 7: Nyquist plots for the corrosion inhibition of mild steel in 1N Hydrochloric acid in the absence and presence of inhibitors

The impedance diagrams are almost semi-circular. The charge transfer resistance values are calculated from the differences in impedance at lower and higher frequencies. The double layer capacitance values are obtained from the frequency at which imaginary component of the impedance ($-Z^{11}_{max}$) is maximum. The relationship used is :

$$f\ (-Z^{11}_{max}) = 1/(2\Pi C_{dl}R_t)$$

It is evident from the Table 5 that R_t value increases with increase in concentration and reaches a limiting value for the mixture of inhibitors. The data also indicate that C_{dl} value decreases with increase in concentration of the inhibitors. The decrease is due to the adsorption of mixture of starch and DPMP on the metal surface.
The efficiency of the inhibitors is calculated directly by using the following relationship [38]:

$$\text{Inhibition Efficiency} = (R_t^{-1}-R_{(inh)}^{-1}) / Rt^{-1}$$

Where $R_{(inh)}^{-1}$ is the charge transfer resistance of the inhibited acid.

Table 5: AC Impedance parameter for the corrosion inhibition of mild steel in 1 N hydrochloric acid with and without inhibitors

Sl.No	Conentration	R_t (ohms)	C_{dl}(μF)	I.E(%)
1.	Blank(HCl)	11.06	0.670	----
2.	0.4 mM starch	30.0	0.661	63.1
3.	0.2 mM DPMP	33.2	0.632	66.6
4.	0.4 mM starch + 0.2 mM DPMP	34.8	0.587	69.6

3.8. FT-IR Spectra

Figure 8 (a) represents the FT-IR spectra of pure DPMP. The IR spectra of pure DPMP molecules shows a strong –NH vibrational stretching frequency at 3294 cm^{-1} and carbonyl stretching frequency at 1689 cm^{-1}. In the FT-IR spectra of mild steel dipped in 1 N Hydrochloric acid containing mixture of starch and DPMP [Figure 8 (b)], the –NH vibrational stretching frequency of DPMP is lowered to 2993 cm^{-1}, which is due to the interaction of –NH group of DPMP with the metal surface. This supports the formation of bond between the metal surface and – NH group of DPMP.

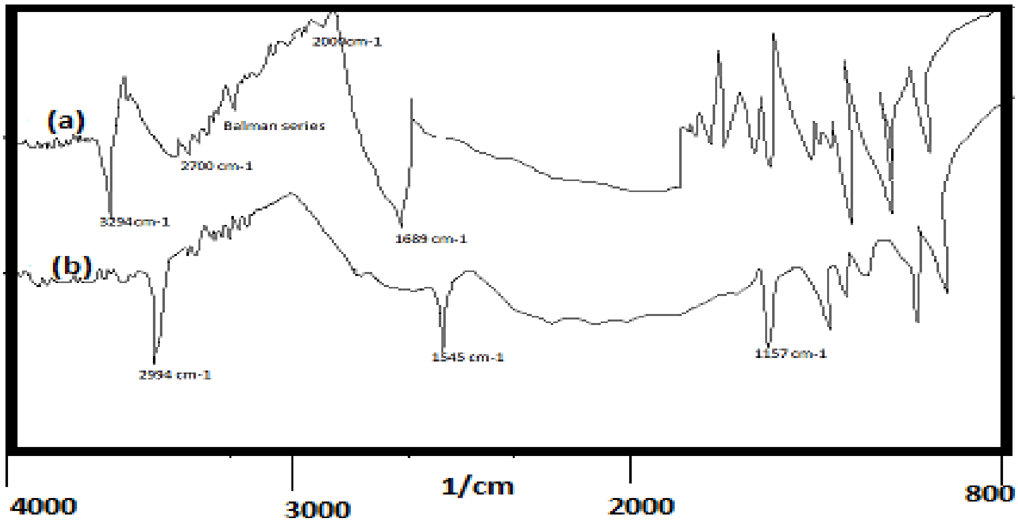


Figure 8: (a) FT-IR Spectra of pure DPMP molecules (b)specimen containing mixture of starch and DPMP

The C-O stretching frequency of glucose unit of starch is lowered to 1157 $cm^{-1,}$ which is a lower shift comparing to the C-O stretching frequency of spectra containing starch alone [39], this indicates that the C=O group of DPMP form a weak hydrogen bonding with the primary hydroxyl group of the glucose units of starch which is most reactive than anomeric carbon based hydroxyl group, causes the weakening of its C-O group. Due to the formation of hydrogen bonding, C=O stretching frequency of DPMP molecule was also lowered to 1543 cm^{-1}. This result concludes that the adsorption of DPMP on the metal surface is through ring nitrogen. The hydrogen bond is formed between the carbonyl group which is para to ring nitrogen in DPMP and primary hydroxyl group of glucose molecule. Thus, FT-IR is a strong evidence for the formation of protective layer by DPMP and glucose units of starch on the mild steel specimen. The adsorption of inhibitors on the metal surface is diagrammatically represented in Figure 9.

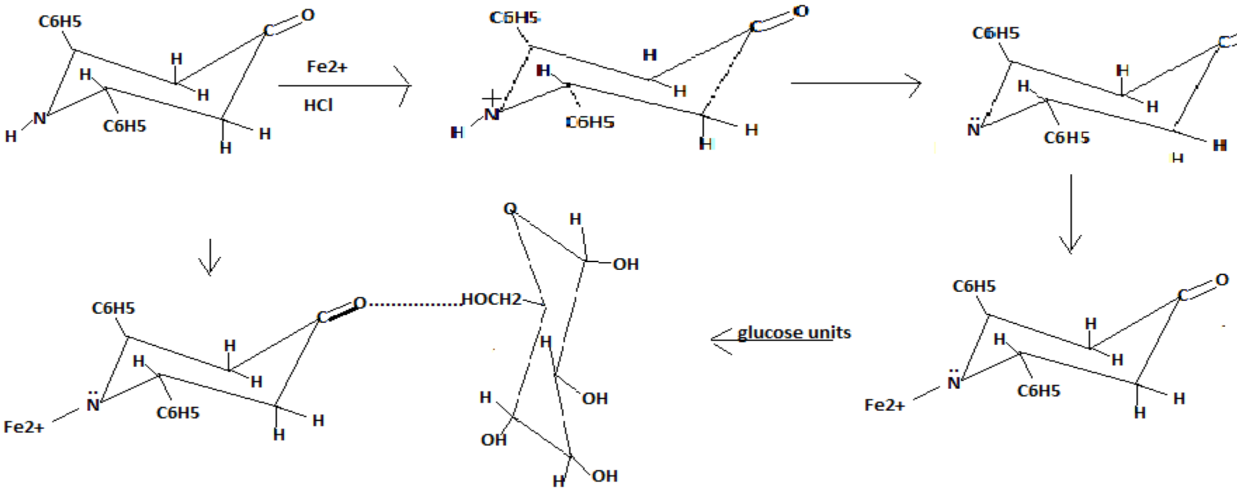


Figure 9: Representation of formation of film on mild steel surface by the mixture of starch and DPMP

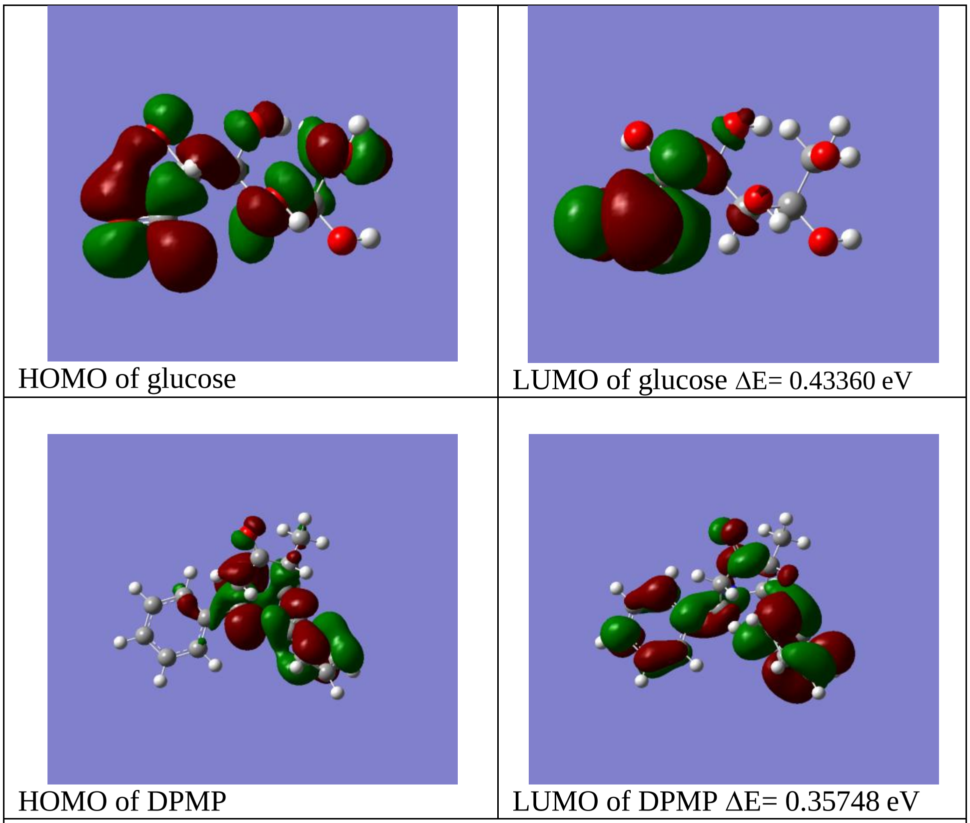
3.9. Quantum chemical studies

Quantum chemical calculations are proven to be very useful tool to understand the corrosion inhibition mechanism and to emphasis the experimental data [40- 44]. According to Frontier Molecular orbital (FMO) theory, the energy values of LUMO, HOMO and their energy gap is related to the chemical reactivity of the reacting species. The absorption of electrons corresponds to the transition of electron from highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) [45]. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are computed at B3LYP/6- 31 G (d) level of theory. The HOMO as an electron donator represents the ability to donate electrons to the empty molecular orbital and LUMO as an electron acceptor represents the ability to accept electrons. HOMO and LUMO energies for DPMP and glucose are calculated and the values are given in Table 6. The higher the value of HOMO the greater is its ease of donating electrons to the empty d orbital of the metal surface and greater its inhibition efficiency [46]. Table 6 clearly shows that the glucose has lowest HOMO energy compared to that of DPMP. Thus, first and foremost DPMP gets protonated in the corrosive medium and donates electrons to the metal surface.

Table 6: HOMO and LUMO energies of glucose and DPMP calculated using B3LYP/ 6-31G (d)

S.NO	Quantum chemical parameters	Glucose	DPMP
1.	E_{HOMO} (eV)	-0.41688	-0.32537
2.	E_{LUMO} (eV)	0.02272	0.03211
3.	ΔE(eV)	0.43360	0.35748

The energy gap values ($\Delta E = E_{LUMO} - E_{HOMO}$) are calculated and MO diagrams for DPMP and glucose are given in the Figures 10 & 11. The reactivity of the molecule increases as ΔE decreases, leading to increase in the inhibition efficiency [47]. Smaller the energy gap, the easier the excitation of electrons. Figure indicates that the HOMO- LUMO energy gap of DPMP is lower compared to the energy gap of glucose. From the energy gap values, it is clear that the primarily DPMP adheres to the metal surface followed by glucose. The expectation is in good agreement with the experimental observations.



HOMO of glucose

LUMO of glucose ΔE= 0.43360 eV

HOMO of DPMP

LUMO of DPMP ΔE= 0.35748 eV

Figure 10: Representation of energy gap value for glucose and DPMP

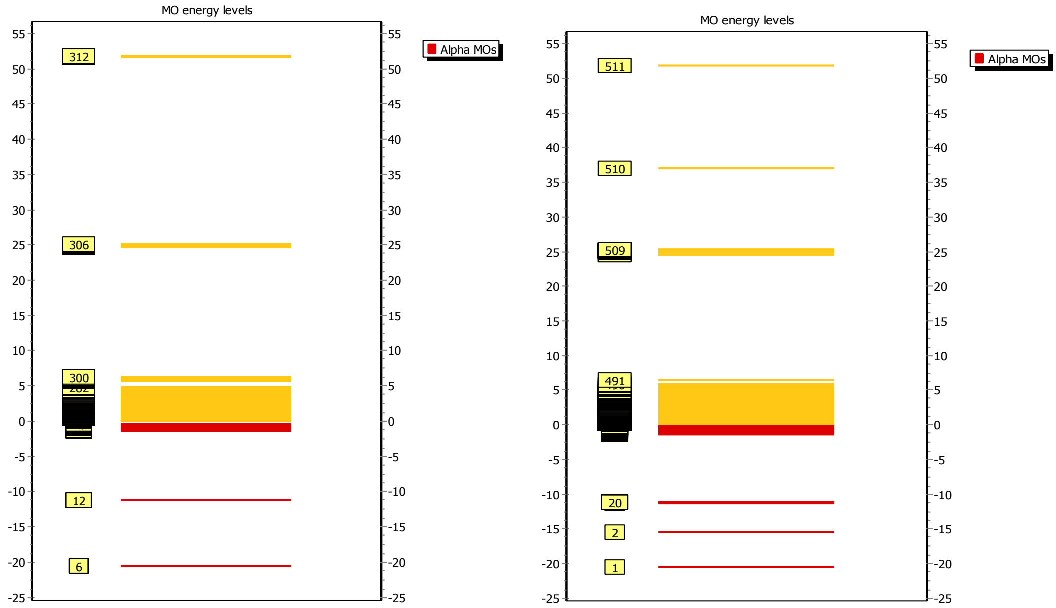


Figure 11: MO plots for glucose and DPMP respectively

Conclusion

1. Starch and DPMP of 2:1 ratio behaves as good corrosion inhibitors for mild steel in 1 N Hydrochloric acid.
2. The effect of DPMP on the corrosion behaviour of starch appears to be synergistic in nature. They both together form a protective layer on the surface of the mild steel.
3. Even though the inhibition efficiency is ≈72%, it is very stable towards higher temperatures at lower concentrations (0.4 mM starch+ 0.2 mM DPMP)
4. The inhibition efficiency is sustainable even after 24 h of immersion. This behaviour is mainly attributed to the strong interaction of the active groups of both the molecules with the metallic surface.

5. The electrochemical studies reveal that the mixture of starch and DPMP acts as a mixed type of inhibitor.
6. The FT-IR spectra show that starch along with DPMP can be used as potential corrosion inhibitor for mild steel in acidic medium.
7. The proposed adsorption nature is supported by the quantum chemical studies.

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