

# Hydrocolloids as intensifying agents in Piperidin-4-one for the corrosion protection of mild steel in 1 mol L<sup>-1</sup> HCl

T. Brindha<sup>\*1</sup> and K. Parimalagandhi<sup>1</sup>

<sup>1</sup>Department of Chemistry, Nehru Institute of Engineering and Technology, Coimbatore, Tamil Nadu, India -641105

<sup>\*1</sup>brindhuchem@gmail.com <sup>1</sup>senparimadhu11@gmail.com

## Abstract

The present work deals with the evaluation of corrosion inhibitive properties of starch (hydrocolloids) and its combination with 2,6 diphenyl piperidin-4-one on mild steel 1 mol L<sup>-1</sup> HCl using weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy methods. The effect of temperature (303-328 ± 1 K) inhibition of corrosion has also been studied. The corresponding corrosion kinetic parameters were calculated and discussed. Potentiodynamic polarization and electrochemical impedance studies were also carried out to determine its the corrosion behaviour on mild steel.

**Key words:** starch, corrosion inhibition, mild steel

## 1. INTRODUCTION

The corrosion of iron and steel is a subject of academic and industrial concern and has received a substantial amount of attention. The use of corrosion inhibitor is one of the most practical methods for the mild steel protection. The corrosion inhibitors are generally used to protect metals against the attack of the acid solutions, which are widely used in acid pickling, industrial cleaning, acid descaling, and oil well acidizing, *etc.* The acid pickling of mild steel in various industries is generally carried out at higher temperatures. In order to reduce the rate of metal attack and acid

consumption, corrosion inhibitors are added to the solution during pickling process. The added corrosion inhibitors reduce the corrosion rate either by adsorption or forming a protective film/insoluble complex. They adsorbed onto the mild steel surface either through the multiple bonds present in the inhibitor molecules or the heteroatoms such as nitrogen, sulphur, oxygen *etc.*

In recent times, number of polymers have been exploited as corrosion inhibitors due to their inherent strength and cost efficacy. The functional group of polymers form complexes with metal ions, which occupy a larger surface area and thus protects the metals from corrosive attack [1,2]. The corrosive inhibitive properties of polyethylene glycol, polyvinyl alcohol, polyvinyl pyridine, polyvinyl pyrrolidone, polyethylenimine, polyacrylic acid and polyacrylamide have been already reported ([3]-[6]). Literature survey clearly shows that, number of naturally occurring materials have shown promising results as corrosion inhibitors for iron and mild steel in acidic solutions ([7]-[10]). It was found that starch with surfactants can be used as potential corrosion inhibitor on mild steel in acidic medium [2]. The corrosion resistance of tapioca starch on AA6061 alloy in marine

environment was investigated by Rosliza and Wan Nick [11]. More recently, modified cassava starches were evaluated as corrosion inhibitor for carbon steel in alkaline solutions [2]. The abundant availability at low cost and biodegradable nature of starch (hydrocolloids), made it as better corrosion inhibitor. Chemically it is a polysaccharide consisting of a large number of glucose units joined together by glycosidic linkages. It contains two structurally different components namely, amylose (15-20%) and amylopectin (80-85%). The amylose is composed of large linear chain of  $\alpha$  (1-4) linked  $\alpha$ -D-glucopyranosyl residue, whereas amylopectin is a branching form of  $\alpha$ -glycon linked by  $\alpha$  (1-6) linkages. The molecular structure of starch suggests that it has strong potential to act as an effective corrosion inhibitor. The majority of the acid corrosion inhibitors have been known for their specificity of inhibition action. The corrosive inhibitive properties of starch depend on the type and functional groups present in it [12]. A combination of inhibitors is likely to provide multiple effects required for effective corrosion inhibition. 2,6 diphenylpiperidin-4-one (DPP) with two potential anchoring sites act as very good corrosion inhibitors in acidic medium [13]. Hydrocolloids are expected to intensify the corrosion inhibition characterization of DPP on mild steel in hydrochloric acid solution.

## II. MATERIAL AND METHODS

### A. Purification of starch

Commercially available starch was purchased from Sigma Aldrich. 250 g of starch was slurried

in 1 litre of double distilled water with occasional stirring for 1 h. The starch solids were collected and filtrated in a Buchner funnel and then washed several times with double distilled water. The purified starch was dried in oven at 40°C. Pure powder of starch was collected.

### B. Synthesis of 2,6-diphenyl piperidin-4-one (DPP)

A mixture of acetone, benzaldehyde, ethanol an ammonium acetate were heated with constant stirring till the colour of the mixture changed to pale orange. The mixture was cooled under running tap water and poured into ether. The ether insoluble 2, 4, 6, 8-tetraphenyl-3,7-diazabicyclo nanan-9-one (m.p.234-236°C) was filtered off and concentrated HCl was added to the filtrate. The precipitated 2,6-diphenyl piperidin-4-one hydrochloride was collected by filtration and recrystallized from ethanol and then dry ether was added until turbidity appeared in the cold solution. The hydrochloride (m.p. 215 - 216°C) was dispersed in acetone and concentrated aqueous ammonia was added drop wise until a clear solution obtained. The clear solution was then poured into crushed ice and the solid precipitate was collected and recrystallized from ethanol. m.p.103-104°C (102-105°C), yield 20 %.

### C. Preparation of mild steel specimens

Mild steel sheets cut into rectangular coupons of size 5 X 1cm<sup>2</sup> provided with holes to enable suspension in test solutions were used for the study. These steel pieces were mechanically polished to remove any rust on it. The metal pieces were then

degreased with acetone washed with distilled water and polished with emery paper, cleaned, dried and stored in desiccators.

*D. Methods*

Metal samples were weighed using electronic balance. Weighed rectangular coupons of the metal samples were immersed in triplicate in 100 mL of 1 mol L<sup>-1</sup> HCl with different concentrations of starch, DPP and the mixture. After 1 hour immersion in the test solution the coupons were removed washed, dried and weighed. Weight loss was measured for all the above mentioned timings at 303K. Corrosion inhibition studies were also carried out at different temperatures (303 to 328 ± 1K). Corrosion rate and inhibition efficiency were calculated using the formulae given in equation (1.1) and (1.2).

$$\text{Corrosion rate (mmpy)} = 87.6 \times \frac{W}{\rho At} \quad (1.1)$$

where, W - weight loss (g), ρ - density of the mild steel specimen (g cm<sup>-3</sup>), A - area of specimen (cm<sup>2</sup>) and t - time of exposure (h).

$$\text{Inhibition efficiency (\%)} = 1 - \frac{W_i}{W_o} \times 100 \quad (1.2)$$

where, W<sub>i</sub> and W<sub>o</sub> are the weight losses of mild steel in inhibited and uninhibited solution respectively.

The surface coverage (θ) has been calculated using the formula

$$\text{Surface coverage } (\theta) = \frac{W_o - W_i}{W_o} \quad (1.3)$$

III. RESULTS AND DISCUSSION

A. Weight loss measurements

1. Corrosion inhibition performance of starch on mild steel in 1 mol L<sup>-1</sup> HCl

The corrosion of mild steel in 1 mol L<sup>-1</sup> HCl in the absence and presence of various concentrations of starch was studied using weight loss method at 303 ± 1 K. The plot of inhibition efficiency as a function of concentration of starch is given in Fig 1.

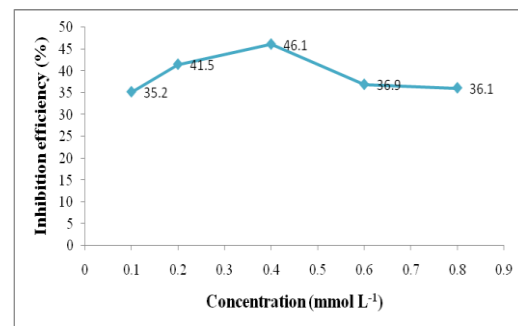


Fig.1 Plot of concentration of starch versus inhibition efficiency on mild steel in 1 mol L<sup>-1</sup> HCl

The inhibition efficiency of starch increases with increase in its concentration showing a maximum efficiency of 46.1 % for 0.4 mmol L<sup>-1</sup>. Further addition of starch does not significantly influence the inhibition efficiency. The inhibition of mild steel corrosion in the presence of starch could be attributed to the adsorption of starch onto the mild steel surface by forming a protective film, which acts as a barrier between the mild steel surface and corrosive medium [2,7]. In acid solutions, starch may be partially hydrolyzed into simpler carbohydrates namely D-glucose. The structure of D-glucose can be either in an open-chain or a ring form. The interaction of starch/hydrolyzed starch on the mild steel surface

takes place through the donation of lone pair of electrons of the oxygen atom and thus facilitates the adsorption process [2].

2. Corrosion inhibition performance of DPP

The corrosion of mild steel in 1 mol L<sup>-1</sup> HCl in the absence and presence of DPP were studied using weight loss method at 303 ±1 K. The inhibition efficiency (%), corrosion rate (mmpy) and surface coverage (θ) at different concentrations were calculated and the results are given in Table 1.

TABLE 1  
Corrosion parameters for mild steel in 1 mol L<sup>-1</sup> HCl in the absence and presence of DPP obtained from weight loss measurements

Concentration (mmol L <sup>-1</sup> )	Inhibition efficiency (%)	Corrosion rate (mmpy)	Surface coverage (θ)
0.2	68.7	0.0283	0.687
0.4	71.1	0.0264	0.711
0.6	75.0	0.0227	0.750
0.8	76.7	0.0215	0.767

Analysis of Table 1 reveals that the inhibition efficiency of DPP increases and corrosion rate decreases with increase in the concentration of the inhibitors. The inhibition efficiency depends on the substitution at *c*-3 position and *c*-3,5 positions of the DPP. This compound exists as an equilibrium mixture of both boat and chair conformations [14] with two anchoring sites namely carbonyl oxygen and ring nitrogen that are para position to each other. The interaction of DPP with the metal surface could

occur either through the carbonyl group or ring nitrogen (chair form) or through the both (boat form) ([15]-[17]). In addition, phenyl rings present in the *c*-2,6 positions flank the ring nitrogen, which plays an important role in the corrosion inhibition of mild steel. These phenyl rings are in equatorial positions, lie parallel to the mild steel surface in chair conformation [18]. The interaction of π electrons of the phenyl rings with the mild steel surface also enhances the corrosion inhibition.

3. Corrosion inhibition performance of starch in the presence of piperidin-4-one derivatives

The spontaneous dissolution of mild steel in 1 mol L<sup>-1</sup> HCl containing different concentrations of hydrocolloids in combination with DPP was studied by weight loss measurements at 303 ±1 K for 1 hour immersion period. The calculated values of inhibition efficiency (%), corrosion rate (mmpy) and surface coverage (θ) are given in Table 2.

TABLE 2  
Corrosion parameters for the various combinations of hydrocolloid and DPP on mild steel in 1 mol L<sup>-1</sup> HCl

Concentration (mmol L <sup>-1</sup> )		Corrosion parameters		
DPP	Hydrocolloid	Inhibition efficiency (%)	Corrosion rate (mmpy)	Surface coverage (θ)
0.2	0.2	75.4	0.00072	0.75
0.4	0.2	85.7	0.00041	0.86
0.6	0.2	85.2	0.00044	0.85
0.8	0.2	84.8	0.00045	0.85

Analyses of the data in table clearly show that the corrosion rate and inhibition efficiency of the each system primarily depends on the conformation of the DPP. Interestingly, the inhibition efficiency offered by the inhibitor mixture in 1 mol L<sup>-1</sup> HCl is higher than that of the individual performance of hydrocolloid and DPP. Increasing the concentration of hydrocolloid from 0.2 mmol L<sup>-1</sup> to 0.4 mmol L<sup>-1</sup> does not make remarkable change in the inhibition efficiency. The maximum inhibition efficiency of 85.7 % is obtained for the inhibitor mixture containing hydrocolloid (0.2 mmol L<sup>-1</sup>) and DPP (0.4 mmol L<sup>-1</sup>), which is higher than the individual performance of starch (41.5 %) 0.4 mmol L<sup>-1</sup> of DPP (71.1 %). The interaction of inhibitor mixture with the mild steel surface may take place through any one of the following mechanisms.

- i. As the inhibitor mixture is added to the corrosive medium containing 1 mol L<sup>-1</sup> HCl, the interaction of DPP with the mild steel surface could occur through both the carbonyl and ring nitrogen (boat form). Then the primary hydroxyl group of unhydrolysed starch molecules present in the same medium forms weak hydrogen bonding with the already adsorbed piperidin-4-one molecule.
- ii. The simultaneous adsorption of DPP through ring nitrogen/carbonyl oxygen and hydrolysed starch through lone pair electrons of oxygen atom on the mild steel surface.
- iii. Combination of above two processes on the mild steel surface.

*B. Effect of Temperature*

The effect of temperature on inhibition reaction is highly complex. This may be due to any one or combination of rapid etching, rupture, desorption of inhibitor and decomposition and/or rearrangement of inhibitor. For this purpose selected combinations of starch and DPP that gives maximum efficiency at 303 ± 1 K are studied for its temperature effect and named as inhibitor mixture (OIS).

The present study was aimed at exploring the activation energy and adsorption nature of the corrosion process of the selected inhibitor systems on mild steel in 1 mol L<sup>-1</sup> HCl using weight loss measurement at 303-328 ± 1 K for 1 h immersion time (Fig 2). It is evident that, a decrease in inhibition efficiency with increasing temperature suggests possible desorption of the adsorbed molecules from the mild steel surface at higher temperatures.

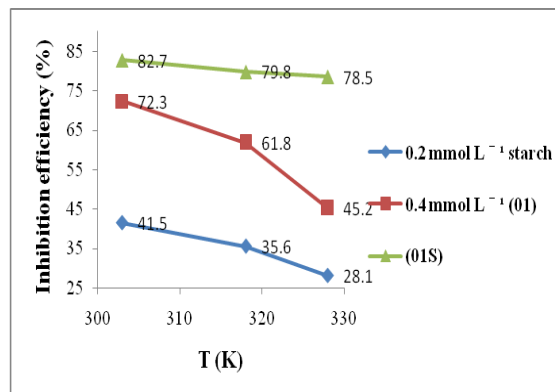


Fig. 2. Plot of inhibition efficiency versus different temperatures for mild steel in 1 mol L<sup>-1</sup> HCl in the presence of inhibitors and inhibitor mixture

The corrosion rates of mild steel in 1 mol L<sup>-1</sup> HCl in the presence of mixture are reduced in comparison to hydrocolloid and DPP alone. The

amount of desorption is comparatively less in the presence of binary inhibitors than the individual inhibitors. At 318 and 328 ±1 K, starch (0.2 mmol L<sup>-1</sup>) exhibits an inhibition efficiency of 35.6 and 28.1%, respectively and DPP (0.4 mmol L<sup>-1</sup>) shows inhibition efficiency of 61.8 and 45.2 %, respectively. But in the inhibitor mixture (OIS), inhibition efficiency of 79.8 and 78.5 % were obtained at the same temperature range studied. The results clearly reveal novel usage of starch as intensifying agent in DPP, which possess excellent corrosion inhibitive properties and can be applied at both the room and higher temperature limits. Apparently, the results obtained postulate that the functions through adsorption on the metallic surface by the blocking the active sites to form a thin film on the mild steel surface and thereby protects from the acidic solution.

The temperature effect on the corrosion kinetics process in the absence and presence of inhibitors leads to obtain more information on the kinetic behaviour of materials in aggressive media [19]. The dependence of corrosion rate on temperature is given by the Arrhenius equation:

$$\log CR = \log A - \frac{E_a^*}{2.303 RT} \quad (3.1)$$

where, 'CR' is the corrosion rate determined from the weight loss measurement, 'E<sub>a</sub><sup>\*</sup>' the apparent activation energy, 'A' the Arrhenius constant, 'R' the molar gas constant and 'T' the absolute temperature.

The apparent activation energy for all the studied systems were determined by the linear

regression between log CR and 1/ T and the corresponding plots are given in Fig 3.

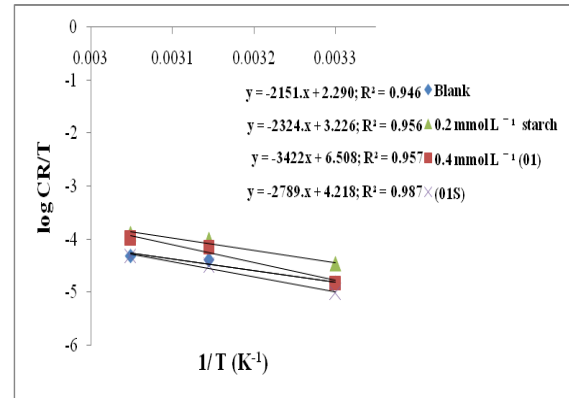


Fig 3. Arrhenius plots for corrosion inhibition of mild steel in 1 mol L<sup>-1</sup> HCl with and without inhibitors, and inhibitor mixture

From the slope ( $-E_a^*/2.303R$ ), the values of activation energy were calculated and given in Table 3. It is noteworthy that the presence of each inhibitor changes the apparent activation energy values. The  $E_{a(\text{blank})}^*$  is found to be 43.8 kJ mol<sup>-1</sup>. The values of  $E_{a(\text{starch})}^*$ ,  $E_{a(\text{DPP})}^*$  and  $E_{a(\text{OIS})}^*$  are 47.1, 48.9 and 44.0 kJ mol<sup>-1</sup> respectively. It is clear that activation energies for the inhibited solutions are higher than blank. The increase in apparent activation energy in the inhibited solution suggests physical adsorption and this can be attributed to an appreciable decrease in the adsorption of the inhibitor on the mild steel surface with increase in temperature. As temperature increases more desorption of inhibitor molecules occur from the mild steel surface. Due to the greater surface area of mild steel comes in contact with corrosive

medium results in an increase in corrosion rates with increase in temperature [20]. The adsorption of these inhibitors occur on the higher energy sites (active sites), must be associated with an increase in the activation energy of mild steel corrosion [21].

TABLE 3

Activation parameters  $E_a^*$ ,  $\Delta H^*$  and  $\Delta S^*$  for the mild steel in 1 mol L<sup>-1</sup> HCl with and without inhibitors, and binary inhibitors

System/ Concentration	Activation parameters			
	From Arrhenius plots	From transition state plots		
	$E_a^*$ (kJ mol <sup>-1</sup> )	$\Delta H^*$ (kJ mol <sup>-1</sup> )	$\Delta S^*$ (J K <sup>-1</sup> mol <sup>-1</sup> )	$E_a - \Delta H^*$ (kJ mol <sup>-1</sup> )
Blank (1 mol L <sup>-1</sup> HCl)	43.8	41.2	-142.6	2.6
0.2 mmol L <sup>-1</sup> starch	47.1	44.4	-135.9	2.6
0.4 mmol L <sup>-1</sup> (O1)	68.1	65.5	-72.90	2.6
(O1S)	56.0	53.4	-116.8	2.6

Other kinetics data (enthalpy and entropy of corrosion process) were derived using the alternative formulation of the Arrhenius equation [22]:

$$CR = \left(\frac{RT}{Nh}\right) \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(\frac{-\Delta H^*}{RT}\right) \quad (3.2)$$

where, 'h' the Planck's constant, 'N' the Avogadro's number, 'R' the universal gas constant, 'T' the absolute temperature,  $\Delta S^*$  is the entropy of activation and  $\Delta H^*$  is the enthalpy of activation. Fig 4 represent the plot of log (CR/T) versus 1/T

for the corrosion of mild steel in the absence and presence of inhibitors/binary inhibitors in 1 mol L<sup>-1</sup> HCl. They gave straight line with slope ( $-\Delta H^*/2.303 R$ ) and an intercept ( $\log (R/ Nh) + \Delta S^*/2.303 R$ ), from which values of  $\Delta H^*$  and  $\Delta S^*$  were calculated and included in Table 4. In general, the positive values of enthalpy of activation reflect endothermic nature of mild steel dissolution, whereas negative value is a sign of exothermic nature of mild steel dissolution.

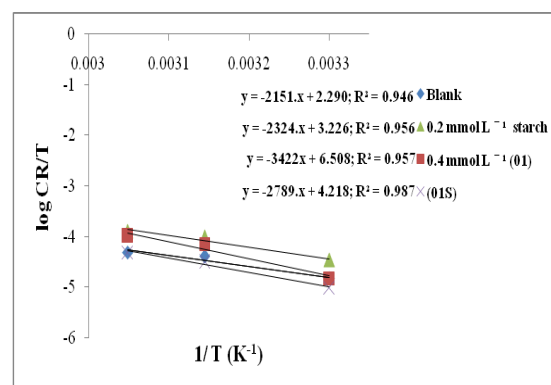


Fig 4. Transition state plots for corrosion inhibition of mild steel in 1 mol L<sup>-1</sup> HCl with and without inhibitors, and inhibitor mixture

A keen sight into the Table 4 clearly shows that  $\Delta H^*$  is positive for all the studied systems reflect the endothermic nature of mild steel dissolution. The positive and negative values of entropy are associated with the phenomenon of ordering and disordering of the inhibitor molecules at the electrode surface and could be explained as follows. The adsorption of inhibitor molecules from the aqueous solution can be regarded as a quasi-substitution process between the inhibitor molecules in the aqueous phase and water

molecules at the electrode surface. The adsorption of inhibitors on the mild steel surface is accompanied by desorption of water molecules from the surface. Thus the exothermic nature of adsorption process is associated with a decrease in entropy and endothermic nature of adsorption process is associated with an increase in entropy. It is also clear from the table that the values of  $\Delta S^*$  are less negative for the inhibited solutions which imply that an increase in disordering takes place on going from reactants to the metal/solution interface [23], which is the driving force for the adsorption of inhibitors onto the mild steel surface.

*C. Potentiodynamic polarization studies*

Potentiodynamic polarization curves for mild steel in 1 mol L<sup>-1</sup> HCl solution at 303 ± 1 K in the absence and presence of starch, DPP and their corresponding inhibitor mixture is shown in Fig 5.

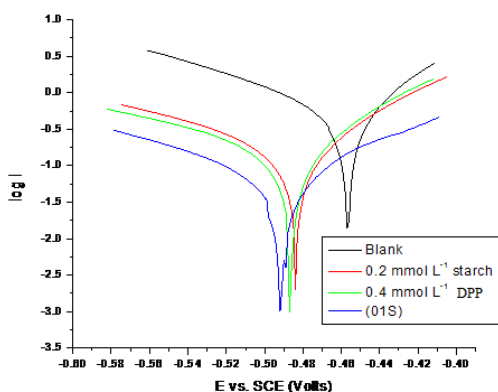


Fig 5 Potentiodynamic polarization curves for mild steel in 1 mol L<sup>-1</sup> HCl in the absence and presence of inhibitors and inhibitor mixture

The calculated electrochemical corrosion parameters such as corrosion current density ( $i_{corr}$ ),

corrosion potential ( $E_{corr}$ ), anodic and cathodic Tafel slopes ( $b_a$  and  $b_c$ , respectively) are presented in Table 4.

TABLE 4  
Potentiodynamic polarization parameters for the corrosion inhibition of mild steel in 1 mol L<sup>-1</sup> HCl with and without inhibitors and, binary inhibitors

System/ Concentration	$i_{corr}$ ( $\times 10^{-4}$ mA cm <sup>-2</sup> )	$E_{corr}$ (mV/S CE)	$b_a$ (mV dec <sup>-1</sup> )	$b_c$ (mV dec <sup>-1</sup> )	IE (%)
Blank (1 mol L <sup>-1</sup> HCl)	0.328	- 467	52	112	-
0.2 mmol L <sup>-1</sup> starch	0.159	- 480	61	119	51.5
0.4 mmol L <sup>-1</sup> (01)	0.153	- 481	57	134	53.3
(01S)	0.073	- 492	88	110	78.0

Analysis of table clearly shows that  $i_{corr}$  decreases considerably in the presence of individual inhibitors and it reaches a minimum value for the binary inhibitors. The  $i_{corr}$  value of the blank is found to be 0.328 mA cm<sup>-2</sup>. For instance, the average difference of  $i_{corr}$  value between blank and 0.2 mmol L<sup>-1</sup> starch is 0.175 mA cm<sup>-2</sup> and that of blank and DPP is 0.169 mA cm<sup>-2</sup>, whereas in the case of inhibitor mixture (01S) the average difference of  $i_{corr}$  is 0.255 mA cm<sup>-2</sup>. These results clearly reveal that the added inhibitors act as an effective corrosion inhibitor on mild steel in 1 mol L<sup>-1</sup> HCl, but the inhibitor mixture are found to have most pronounced effect towards corrosion of mild steel. A keen sight into the Fig clearly shows that the addition of inhibitors/binary inhibitors to the corrosive medium shifts the  $E_{corr}$  towards more



negative side. These results imply that the added inhibitors and binary inhibitors behave as mixed-type inhibitor. Also, shifts were observed in both the anodic and cathodic Tafel slopes, indicating that the studied inhibitor systems under investigation act as efficient corrosion inhibitor, suppressing both anodic dissolution and cathodic hydrogen evolution reaction either by getting adsorbed onto the mild steel surface or blocking the active sites, without altering the mechanism of corrosion reaction. Moreover, the inhibition efficiency for the individual inhibitors and binary inhibitors calculated by the weight loss and polarization measurements are in good agreement. But some differences are observed and this can be attributed to the fact that the weight loss method gives average corrosion rate, whereas the polarization method gives instantaneous corrosion rate [24,25].

*D. Electrochemical impedance spectroscopy*

The corrosion behaviour of mild steel in 1 mol L<sup>-1</sup> HCl in the absence and presence of starch, DPP and their inhibitor mixture were investigated and the impedance parameters R<sub>ct</sub> and C<sub>dl</sub> were calculated and given in Table 5. Their representative Nyquist plots are shown in Fig 6. The impedance diagrams obtained are not perfect semi-circles, and the deviation from the semi-circular nature has been attributed to the frequency dispersion as a result of roughness and inhomogeneties nature of the mild steel surface [26].

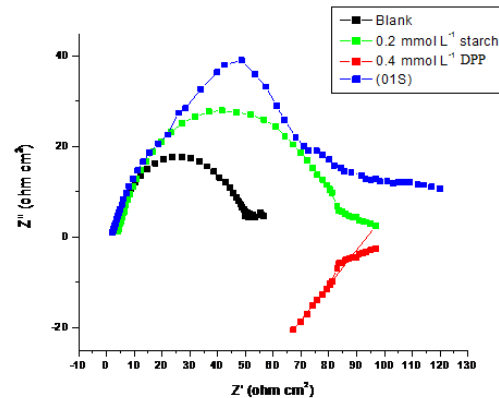


Fig 6 Nyquist plots for mild steel in 1 mol L<sup>-1</sup> HCl in the absence and presence of inhibitors and inhibitor mixture

TABLE 5  
Electrochemical impedance parameters for mild steel in 1 mol L<sup>-1</sup> HCl with and without inhibitors and, binary inhibitors

System/ Concentration	R <sub>ct</sub> (Ω cm <sup>2</sup> )	C <sub>dl</sub> (μF cm <sup>-2</sup> )	Inhibition efficiency (%)
Blank (1 mol L <sup>-1</sup> HCl)	50.9	0.000184	-
0.2 mmol L <sup>-1</sup> starch	95.0	0.000060	46.4
0.4 mmol L <sup>-1</sup> (01)	94.2	0.000062	45.9
(01S)	120.0	0.000042	57.5

Analysis of table clearly reveals that the addition of inhibitors to the corrosive medium causes a significant change in the R<sub>ct</sub> and C<sub>dl</sub> values. The data show that the values of R<sub>ct</sub> are higher in the presence of starch, DPP and it reaches a maximum value for inhibitor mixture (01S) compared to the blank solution. The increase in R<sub>ct</sub> values results in decrease in conductive behaviour of the inhibitors and binary inhibitors, which forms a protective film at the metal/solution interface and this film, makes a blockade for mass transport and

charge-transfer. The decrease in  $C_{dl}$  values results from the adsorption of the inhibitor molecules at the metal surface. The double layer existing between the charged mild steel surface and the corrosive medium is considered as an electrical capacitor. The adsorption of inhibitors/binary inhibitors on the mild steel surface decreases the double layer's electrical capacity as they displace the water molecules and other ions originally adsorbed on the surface leading to the formation of a protective film on the electrode surface which increases the thickness of the electrical double layer. The thickness of this protective layer ( $d$ ) is related to  $C_{dl}$  in accordance with Helmholtz model, as given by equation (3.3)

$$C_{dl} = \frac{\epsilon\epsilon_0 A}{d} \quad (3.3)$$

where, ' $\epsilon$ ' is the dielectric constant of the medium and ' $\epsilon_0$ ' is the permittivity of the free space ( $8.854 \times 10^{-14}$  F/cm) and ' $A$ ' is the effective surface area of the electrode. From the above equation, it is clear that as the thickness of the protective layer/film formed by the inhibitor molecules/ inhibitor mixtures increases, the  $C_{dl}$  should decrease. In the present studies,  $C_{dl}$  value is found to be higher for the uninhibited solution and the most pronounced decrease is observed in the case of binary inhibitors. The decrease in the  $C_{dl}$ , results from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, suggests that the inhibitors as well as binary inhibitors function by adsorption at the metal/solution interface. The decrease in double layer capacitance may results from the adsorption

of inhibitors and the binary systems on the surface of the outer Helmholtz plane and decreases its electrical capacity. Further, the calculated inhibition efficiency is in good agreement with those obtained from polarization studies.

#### IV. CONCLUSION

The inhibition efficiency of starch increases with increase in the concentration. The interaction of starch on the mild steel surface takes place through the donation of lone pair electrons of the oxygen atom. The inhibition efficiency of DPP also increases with increase in the concentration. The inhibition efficiency depends on the substitution at *c*-3 position and *c*-3,5 positions of the *r*-2,*c*-6-diphenylpiperidin-4-one (DPP). The corrosion and adsorption characteristics of starch in the presence of DPP were also investigated. The inhibition performance shown by all the inhibitor mixture (OIS) on mild steel in 1 mol L<sup>-1</sup> HCl is higher than that of the individual performance of starch and DPP. However, the inhibitor mixture (OIS) is found to exhibit highest inhibition efficiency which is due to the boat conformation of *r*-2,*c*-6-diphenylpiperidin-4-one (DPP). Corrosion kinetic parameters clearly show that physical mode of adsorption is favoured for inhibitors/binary inhibitors on the mild steel surface. Electrochemical studies clearly reveal that the added inhibitors (starch and DPP) and inhibitor mixture (OIS) acts as mixed-type inhibitor. Thus all the studies concludes that starch intensifies the

corrosion inhibition characterization of DPP on mild steel in hydrochloric acid solution.

## REFERENCES

1. Rajendran, N.S., Sridevi, S.P., Anthony, N and Amalraj, N. (2005): Anti-corrosion Methods and Materials, **52**, 10237.
2. Mobin, M., Khan, M.A and Parveen, M. (2011): Journal of Applied Polymer Science, **121**, 1558.
3. Abed, Y., Arrar., Z Aounit, A., Hammouti, B., Kertit, S and Mansri, A. (1997): Journal of Chemical Physics, **95**, 1347.
4. Jianguo, Y., Lin, W.Y., Otieno-Alego, V and Schweinsberg, D.P. (1995): Corrosion Science, **37**, 975.
5. Schweinsberg, D.P., Hope, G.A., Trueman, A and Otieno-Alego, V. (1996): Corrosion Science, **38**, 587.
6. Abed, Y., Arrar., Z Aounit, A., Hammouti, B., Kertit, S and Mansri, A. (2001): Anti-corrosion Methods and Materials, **48**, 304.
7. Etre, A.Y. (1998): Corrosion Science, **40**, 1845.
8. Etre, A.Y., and Abdallah, M. (2000): Corrosion Science, **42**, 731.
9. Abdallah, M. (2004): Portugaliae Electrochimica Acta, **22**, 161.
10. Etre., A.Y. (2003): Corrosion Science, **45**, 2485.
11. Rosliza, R., and Wan Nik, W.B. (2009): *Current Applied Physics*, **10**, 221.
12. Bello, M., Ochoa, N., Balsoma, V., Lopez-carrasquero, F., Coll, S., Monsalve, A., and Gonzalez, G. (2010): Carbohydrate Polymers, **82**, 561.
13. Abd El Haleem, S.M., Abd El Rehim, S.S, and Shalaby, M. (1986): Surface Coatings and Technology, **27**, 167.
14. Glory, T.X., Brindha , T and Mallika, J. (2015): International Journal of Corrosion, **2015**, 15.
15. Vijayan, B. Ph.D Thesis, Annamalai University, Chidambaram, India, (1981).
16. Sankarapavinasam, S., Pushpanaden, F and Ahmed, M.F. (1991): Corrosion Science, **32**, 193.
17. Muralidharan, S., Chandrasekar, R and Iyer, S.V.K. (2000): Proceedings of Indian academy Sciences (Chemical Sciences), **112**, 127.
18. Senthilkumar, A.N., Tharini, K and Sethuraman, M.G. (2009): Surface Review and Letters, **16**, 141.
19. Senthilkumar, A.N., Tharini, K and Sethuraman, M.G. (2010): Journal of Materials Engineering and Performance, **20**, 969.
20. Khaled, K.F., Samardzija, K.B and Hackerman, N. (2004): Journal of Applied Electrochemistry, **34**, 697.
21. Rao, V.S., and Singhal, L.K. (2009): Journal of Materials Science, **44**, 2327.
22. Samardzija, K.B., Khaled, K.F, and Hackerman, N. (2005): Anti- Corrosion Methods and Materials, **52**, 11.



23. Shukla, S.K., and Ebenso, E.E. (2011):  
International Journal of Electrochemical  
Science, **6**, 3277.
24. Obot, I.B., Egbedi, N.O.O and Umoren,  
S.A. (2009): International Journal of  
Electrochemical Science, **4**, 863.
25. Riggs, O., Hurd, I.R and Ray, M. (1967):  
Corrosion, **23**, 252.
26. Fouda, A.S., Abd El-Aal, A and Kandil,  
A.B. (2006): Desalination, **86**, 201.