

# Binary mixtures of Piperidin-4-one derivatives and polymeric carbohydrate for the corrosion inhibition of mild steel in hydrochloric acid

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**Abstract.** The adsorption and corrosion inhibition characteristics of starch, a polymeric carbohydrate and its combination with piperidin-4-one derivatives (*r*-2, *c*-6-Diphenyl-N-methylpiperidin-4-one, *r*-2) on mild steel 1 mol L<sup>-1</sup> HCl using weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy methods. The inhibition performance shown by all the binary inhibitors (DMP1S & DMP2S) on mild steel in 1 mol L<sup>-1</sup> HCl is higher than that of the individual performance of starch and piperidin-4-one derivatives (DMP1 & DMP2).

**Keywords.** Binary inhibitors; Piperidin-4-one derivatives; Mild steel; polymeric carbohydrates

## 1. Introduction

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<sup>1,2</sup>. The corrosive inhibitive properties of polyethylene glycol, polyvinyl alcohol, polyvinyl pyridine, polyvinyl pyrrolidone, polyethylenimine, polyacrylic acid and polyacrylamide have been already reported<sup>3-6</sup>. Literature survey clearly shows that, the number of naturally occurring materials have shown promising results as corrosion inhibitors for iron and mild steel in acidic solutions<sup>6-9</sup>. Mobin *et al.*<sup>7</sup>, found that starch with surfactants can be used as potential corrosion inhibitor on mild steel in acidic medium. The corrosion resistance of tapioca starch on AA6061 alloy in marine environment was investigated by Rosliza and Wan Nick<sup>10</sup>. More recently, modified cassava starches were evaluated as corrosion inhibitor for carbon steel in alkaline solutions<sup>11</sup>. The abundant availability at low cost and biodegradable nature of starch, 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<sup>12</sup>. A combination of inhibitors is likely to provide multiple effects required for effective corrosion inhibition. Piperidin-4-one derivatives with two potential anchoring sites act as very good corrosion inhibitors in acidic medium<sup>13</sup>. Piperidin-4-one derivatives with starch are expected to enhance the corrosion inhibition ability of starch.

## 2. Materials and Methods

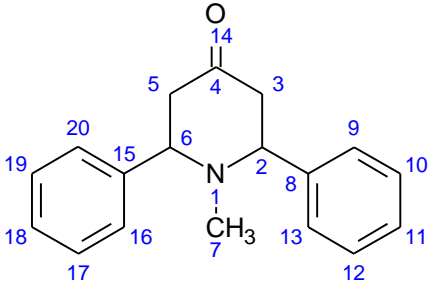
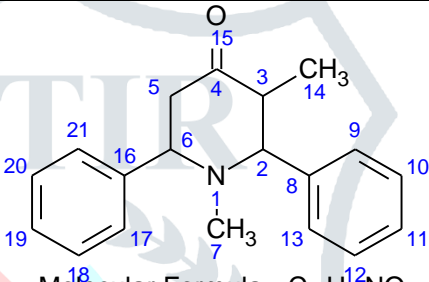
### 2.1. Purification of starch

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.

## 2.2. Synthesis of Piperidin-4-one derivatives

The following Piperidin-4-one derivatives were synthesized following the procedure carried out by Balasubramanian *et al*<sup>14</sup>., Jadhav *et al*<sup>15</sup>., and Osmani *et al*<sup>16</sup>.

- a) *r*-2, *c*-6-Diphenyl-N-methylpiperidin-4-one (DMP1)
- b) *r*-2, *c*-6-Diphenyl-*t*-3,N-methylpiperidin-4-one (DMP2)

<p><b><i>r</i>-2,<i>c</i>-6-Diphenyl-N-methylpiperidin-4-one (DMP1)</b></p>	 <p>Molecular Formula: C<sub>18</sub>H<sub>19</sub>NO Formula Weight: 265.34956 g</p>
<p><b><i>r</i>-2,<i>c</i>-6-Diphenyl-<i>t</i>-3,N-methylpiperidin-4-one (DMP2)</b></p>	 <p>Molecular Formula: C<sub>19</sub>H<sub>21</sub>NO Formula Weight: 279.37614 g</p>

## 2.2. Preparation of specimens

The mild steel specimens used for weight loss measurements were cut to obtain rectangular surfaces with dimensions of 25 x 10 x 1 mm. To immerse in the corrosive medium a hole is drilled at the upper edge of the specimen to hook it in the glass rod. For the electrochemical measurements, the mild steel specimen of the same composition was encapsulated in commercial epoxy resin with an exposure area of 1.0 cm<sup>2</sup>. Substantial layer of the specimen was removed by using various grades of abrasive papers and degreased by scrubbing with bleach-free scouring powder, followed by thorough rinsing in water and acetone.

## 2.4. Preparation of the aggressive medium

The acid solution was prepared by the dilution of AnalaR grade concentrated HCl using double distilled water. The acid was standardized before usage.

## 2.5. Experimental methods

### 2.5.1. Weight loss method

The weight loss measurements were carried out according to the ASTM practice standard G-31<sup>4</sup>.

### 2.5.2. Temperature and Time studies

The effect of temperature (303 - 328 ± 1 K) and immersion time (1, 2, 3, 4, 5 and 24 h) on the corrosion inhibition in the absence and presence of inhibitors on mild steel in acid solution was studied using the same procedure of weight loss measurements.

### 2.5.3. Electrochemical methods

The electrochemical experiments were performed using three-electrode cell assembly. The cell consisted of a platinum counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The working electrode was immersed in the acid solution and the constant steady-state (open circuit) potential was recorded as a function of time, when it became virtually constant.

The electrochemical impedance spectroscopic (EIS) measurements were carried out using AC signals of 10 mV amplitude over the frequency range of 10 KHz to 0.01 Hz. The electrode was immersed in the solution for half an hour before starting the impedance measurements. All the impedance data were automatically controlled by  $Z_{view}$  software and the diagrams were given as Nyquist plots. The charge transfer resistance ( $R_{ct}$ ) values were obtained from the diameter of the semicircles of the Nyquist plots. The inhibition efficiency of the inhibitor was calculated from the charge transfer resistance values according to the following equation (3.4)

$$\text{Inhibition efficiency (\%)} = \frac{R_{ct} - R_{ct}^o}{R_{ct}} \times 100 \quad (4)$$

where,  $R_{ct}$  and  $R_{ct}^o$  are the charge transfer resistance with and without inhibitors, respectively.

The polarization studies were carried out over a potential of + 200 to - 200 mV with respect to the open circuit potential at a scan rate of 1 mV s<sup>-1</sup>. The linear Tafel segments of the cathodic curves and the calculated anodic Tafel lines were extrapolated to the point of intersection to obtain the corrosion potential ( $E_{corr}$ ) and corrosion current density ( $i_{corr}$ ). The inhibition efficiency was evaluated from the measured  $i_{corr}$  values using equation (5)

$$\text{Inhibition efficiency (\%)} = \frac{i_{corr}^o - i_{corr}}{i_{corr}^o} \times 100 \quad (5)$$

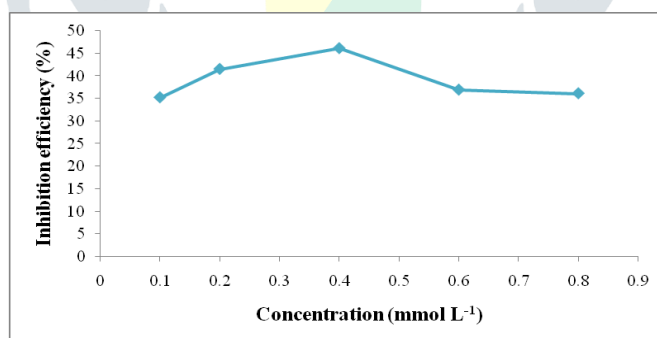
where,  $i_{corr}^o$  is the corrosion current density without inhibitor and  $i_{corr}$  is the corrosion current density with inhibitor.

### 3. Results and Discussion

#### 3.1. Weight loss measurements

##### 3.1.1. 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. Corrosion rate (mmpy), inhibition efficiency (%) and surface coverage ( $\theta$ ) were calculated using the equations (1), (2) and (3), respectively and the results are calculated. The plot of inhibition efficiency as a function of concentration of starch is given in Figure 1.



**Figure 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<sup>3</sup>. 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<sup>3</sup>.

##### 3.1.2. Corrosion inhibition performance of piperidin-4-one derivatives

The corrosion inhibitive effect of mild steel in 1 mol L<sup>-1</sup> HCl in the presence of \_\_\_\_\_ compounds (DMP1&DMP2) has also been investigated and the calculated corrosion parameters are included in Table 1.

**Table 1 Corrosion parameters for mild steel in 1 mol L<sup>-1</sup> HCl in the absence and presence of various concentrations of piperidin-4-one derivatives (DMP1-DMP4) obtained from weight loss measurements**

Inhibitors	Concentration of the inhibitors (mmol L <sup>-1</sup> )	Inhibition efficiency (%)	Corrosion rate in mmpy (g cm <sup>-2</sup> h <sup>-1</sup> )	Degree of surface coverage (θ)
DMP1	0.2	34.2	0.0272	0.342
	0.4	42.4	0.0184	0.424
	0.6	49.6	0.0142	0.496
	0.8	53.8	0.0212	0.538
DMP2	0.2	39.4	0.0162	0.394
	0.4	47.1	0.0144	0.471
	0.6	62.6	0.0098	0.626
	0.8	57.2	0.0083	0.672

Inspection of the table clearly shows that the inhibition efficiency increase with increase in concentration, presence of an electron releasing group at the ring nitrogen induces inductive effect (+I) and thereby increasing the availability of lone pair electrons, which favours increased adsorption on the mild steel surface<sup>17</sup>. On comparing the conformation of *r*-2,*c*-6-diphenyl-*N*-methylpiperidin-4-one (DMP1) with its corresponding piperidin-4-one, the inhibition efficiency of compound (DMP1) was found to less. The decreased inhibition efficiency may be due to its chair conformation<sup>17</sup> in which only one anchoring site is possible towards the adsorption on the mild steel surface. Generally, the +I effect of alkyl group increases in the order methyl < ethyl < propyl. Thus in the case of *r*-2,*c*-6-diphenyl-*t*-3-ethyl-*N*-methylpiperidin-4-one (DMP2), the presence of methyl group makes it to get adsorbed more firmly on the mild steel surface, resulting in highest inhibition efficiency. This may due to the fact that, the domination of buttressing effect over +I effect. Similarly, compounds (DMP1) and (DMP2) with less number of electron releasing groups, possess lower inhibition efficiency.

### 3.1.3. 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 starch in combination with piperidin-4-one derivatives (DMP1-DMP4) 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 Tables 2&3. Analyses of the data in tables clearly show that the corrosion rate and inhibition efficiency of the each system primarily depends on the conformation of the piperidin-4-one derivatives.

**Table 2 Corrosion and synergism parameters for the various combinations of Starch and DMP1 on mild steel in 1 mol L<sup>-1</sup> HCl**

Concentration of the inhibitors (mmol L <sup>-1</sup> )		Corrosion parameters			Synergism parameter (S <sub>i</sub> )
<i>r</i> -2, <i>c</i> -6-diphenyl- <i>N</i> -methylpiperidin-4-one (05)	starch	Inhibition efficiency (%)	Corrosion rate in mmpy (g cm <sup>-2</sup> h <sup>-1</sup> )	Degree of surface coverage (θ)	
0.2	0.2	79.3	0.0029	0.79	1.12
0.4	0.2	75.5	0.0035	0.75	0.94
0.6	0.2	78.9	0.0030	0.79	1.15
0.8	0.2	74.1	0.0037	0.74	1.28

**Table 3 Corrosion and synergism parameters for the various combinations of Starch and DMP2 on mild steel in 1 mol L<sup>-1</sup> HCl**

<i>r</i> -2, <i>c</i> -6-Diphenyl- <i>t</i> -3,N-methylpiperidin-4-one (06) (mmol L <sup>-1</sup> )	Starch (mmol L <sup>-1</sup> )							
	<sup>a</sup> inhibition efficiency ( %), <sup>b</sup> corrosion rate in mmpy (g cm <sup>-2</sup> h <sup>-1</sup> ), <sup>c</sup> degree of surface coverage (θ), <sup>d</sup> synergism parameter (S <sub>i</sub> )							
	0.2		0.4		0.6		0.8	
0.2	<sup>a</sup> (53.4)	<sup>b</sup> (0.0234)	51.0	0.0245	58.3	0.0207	59.0	0.0203
	<sup>c</sup> (0.53)	<sup>d</sup> (1.52)	0.51	1.69	0.58	1.31	0.59	1.28
0.4	51.3	0.0241	57.9	0.0211	58.8	0.0208	58.1	0.0209
	0.51	1.74	0.58	1.62	0.59	1.43	0.58	1.43
0.6	56.5	0.0219	62.4	0.0188	68.2	0.0158	71.4	0.0143
	0.56	1.85	0.62	1.75	0.68	1.46	0.71	1.38
0.8	60.0	0.0200	66.2	0.0165	78.7	0.0105	78.0	0.0109
	0.60	1.65	0.66	1.56	0.79	1.19	0.78	1.19

The interaction of inhibitor mixture with the mild steel surface may take place through any one of the following mechanisms

- As the inhibitor mixture is added to the corrosive medium containing 1 mol L<sup>-1</sup> HCl, the interaction of DMP1 with the mild steel surface. 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.
- The simultaneous adsorption of DMP1 through ring nitrogen/carbonyl oxygen and hydrolysed starch through lone pair electrons of oxygen atom on the mild steel surface.
- Combination of above two processes on the mild steel surface.

Analysis of Table 2 clearly shows that the combination of compound (DMP1) (0.2 mmol L<sup>-1</sup>) with starch (0.2 mmol L<sup>-1</sup>) gives highest inhibition efficiency (79.3%). This is due to the fact that compound containing -CH<sub>3</sub> group at ring nitrogen increases its basicity<sup>18</sup>, thereby increasing the adsorptive ability on the mild steel surface. The heteroatoms of starch in turn forms hydrogen bonding with the (DMP1) which creates a barrier for charge and mass transfers and thus isolate the mild steel surface from further attack of the corrosive medium. Analysis of tables confirms that the addition of even a very small amount of mixtures to the acid solution retards the corrosion rate of the metal and the extent of retardation is concentration dependent.

Thus, the mixture of starch and piperidin-4-one derivatives either adsorbed in the form of film to control the corrosion rate or create a barrier between the mild steel surface and the corrosive medium.

### 3.5. 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, selected piperidin-4-one derivatives (DMP1 and DMP2), and their corresponding binary inhibitors are shown in Figures 2&3. The calculated electrochemical corrosion parameters such as corrosion current density (*i*<sub>corr</sub>), corrosion potential (*E*<sub>corr</sub>), anodic and cathodic Tafel slopes (*b*<sub>a</sub> and *b*<sub>c</sub>, respectively) are presented in Table 4.

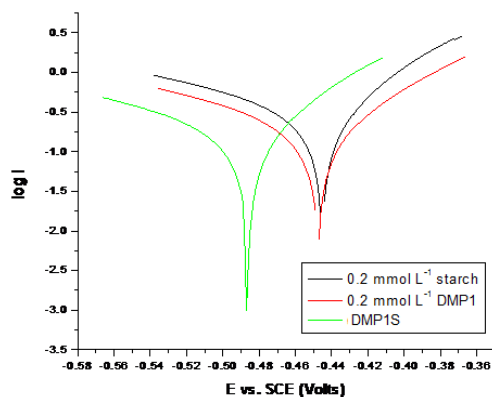


Figure 2 Potentiodynamic polarization curves for mild steel in 1 mol L<sup>-1</sup> HCl in the presence of inhibitors and inhibitor mixtures

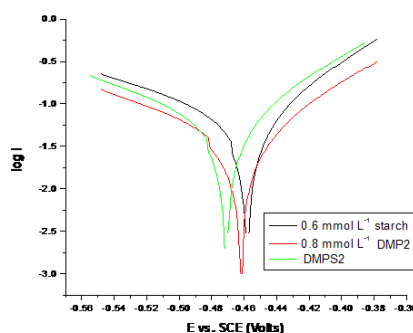


Figure 3 Potentiodynamic polarization curves for mild steel in 1 mol L<sup>-1</sup> HCl in the presence of inhibitors and inhibitor mixtures

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 inhibitor mixtures

System/ Concentration	$i_{\text{corr}}$ ( $\times 10^{-4}$ mA cm <sup>-2</sup> )	$E_{\text{corr}}$ (mV/SCE)	$b_a$ (mV dec <sup>-1</sup> )	$b_c$ (mV dec <sup>-1</sup> )	Inhibition efficiency (%)
Blank (1 mol L <sup>-1</sup> HCl)	0.328	- 467.4	52	112	-
0.2 mmol L <sup>-1</sup> starch	0.159	- 480.3	61	119	51.5
0.2 mmol L <sup>-1</sup> (DMP1)	0.268	- 442.2	58	137	20.0
<b>(DMP1S)</b>	0.168	- 444.4	67	122	48.7
Blank (1 mol L <sup>-1</sup> HCl)	0.328	- 467.4	52	112	-
0.6 mmol L <sup>-1</sup> starch	0.055	- 469.3	72	118	83.2
0.8 mmol L <sup>-1</sup> (DMP2)	0.062	- 453.9	67	133	81.0
<b>(DMP2S)</b>	0.037	- 457.6	7	123	88.7

Analysis of table clearly shows that  $i_{\text{corr}}$  decreases considerably in the presence of individual inhibitors and it reaches a minimum value for the binary inhibitors. The  $i_{\text{corr}}$  value of the blank is found to be 0.328 mA cm<sup>-2</sup>. For instance, the average difference of  $i_{\text{corr}}$  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 DMP1 0.06 mA cm<sup>-2</sup>, whereas in the case of binary inhibitor (DMP1S) the average difference of  $i_{\text{corr}}$  is 0.16 mA cm<sup>-2</sup>. These results clearly reveal that the added inhibitors and the binary inhibitors both act as an effective corrosion inhibitor on mild



steel in 1 mol L<sup>-1</sup> HCl, but the binary inhibitors are found to have most pronounced effect towards corrosion of mild steel. A keen sight into the figures clearly shows that the addition of inhibitors/binary inhibitors to the corrosive medium shifts the E<sub>corr</sub> towards both positive and negative. These results imply that the added inhibitors and binary inhibitors behave as mixed-type inhibitor<sup>18</sup>.

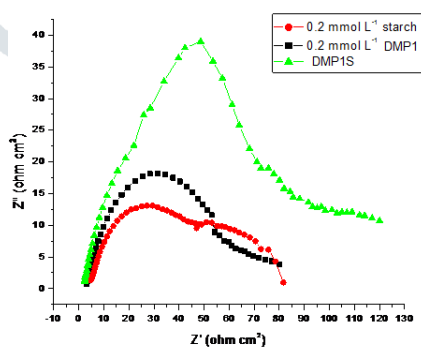
### 3.6. Electrochemical impedance spectroscopy

The corrosion behaviour of mild steel in 1 mol L<sup>-1</sup> HCl in the absence and presence of starch, selected piperidin-4-one derivatives (DMP1 and DMP2) and their corresponding binary inhibitors were investigated and the impedance parameters R<sub>ct</sub> and C<sub>dl</sub> were calculated and given in Table 5

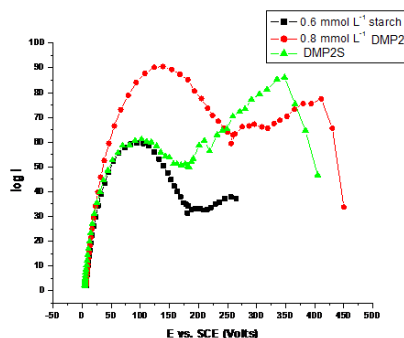
**Table 5 Electrochemical impedance parameters for mild steel in 1 mol L<sup>-1</sup> HCl with and without inhibitors and inhibitor mixtures**

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	0.0001843	-
0.2 mmol L <sup>-1</sup> starch	84.9	0.0001212	40.0
0.2 mmol L <sup>-1</sup> (DMP1)	77.2	0.0001651	34.0
<b>(DMP1S)</b>	117.6	0.0000481	56.7
Blank (1 mol L <sup>-1</sup> HCl)	50.9	0.0001840	-
0.6 mmol L <sup>-1</sup> starch	400.0	0.0000094	87.2
0.8 mmol L <sup>-1</sup> (DMP2)	272.1	0.0000092	81.2
<b>(DMP2S)</b>	449.2	0.0000044	88.6

Their representative Nyquist plots are shown in Figure 4 & 5. 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. The illustrated Nyquist plot is the expected response of the simple circuit given in Figure 6.



**Figure 4 Nyquist plots for mild steel in 1 mol L<sup>-1</sup> HCl in the absence and presence of inhibitors and inhibitor mixture**

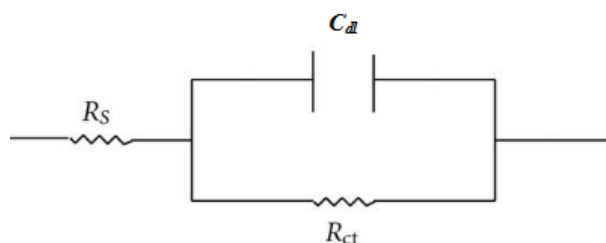


**Figure 5 Nyquist plots for mild steel in 1 mol L<sup>-1</sup> HCl in the absence and presence of inhibitors and inhibitor mixture**

Analysis of table clearly reveals that the addition of inhibitors to the corrosive medium causes a significant change in the  $R_{ct}$  and  $C_{dl}$  values. The data show that the values of  $R_{ct}$  are higher in the presence of starch, piperidin-4-one derivatives and it reaches a maximum value for the binary inhibitors compared to the blank solution. The increase in  $R_{ct}$  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 (9)

$$C_{dl} = \frac{\epsilon\epsilon_0 A}{d} \quad (9)$$

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/binary inhibitors 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.



**Figure 6 Equivalent circuit model for impedance analysis**

#### 4. Conclusions

The corrosion inhibitive property of starch (amylum) and its combination with piperidin-4-one derivatives (DMP1&DMP4) on mild steel in 1 mol L<sup>-1</sup> HCl were evaluated. 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 piperidin-4-one derivatives (DMP1&DMP2) also increases with increase in the concentration. The corrosion and adsorption characteristics of starch in the presence of piperidin-4-



one derivatives were also investigated. The inhibition performance shown by all the binary inhibitors (DMP1S & DMP2S) on mild steel in 1 mol L<sup>-1</sup> HCl is higher than that of the individual performance of starch and piperidin-4-one derivatives (DMP1 & DMP2). However, the binary inhibitor (DMP1S) is found to exhibit highest inhibition efficiency which is due to the boat conformation of r-2, c-6-Diphenyl-N-methylpiperidin-4-one (DMP1). Corrosion kinetic parameters clearly show that physical mode of adsorption is favoured for inhibitors/binary inhibitors on the mild steel surface

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