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The role of functional groups of cysteine molecules on the corrosion inhibition of carbon steel in CO₂-saturated NaCl solution

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ABSTRACT

The role of functional group of cysteine molecules (2-amino-3-mercaptopropanoic acid) on the corrosion inhibition of API 5L X65 carbon steel in CO₂-saturated 0.25 M NaCl solution has been studied using the polarization (Tafel) and impedance (EIS) methods, along by comparison of inhibitory action with alanine and 3-mercaptopropionic acid compounds. The results of this study denote that the mechanism of cysteine inhibition occurs by the formation of an uneven protective film on the surface of the carbon steel. The adsorption of cysteine molecules on the surface of carbon steel comply the Langmuir isotherm and its adsorbed by physical adsorption. The mercapto group plays a role in film formation, while the amine group causes uneven film adsorption on the surface of the carbon steel. Cysteine is classified as an anodic inhibitor with an inhibition efficiency of up to 90% at a concentration of 0.25 mM.

Keyword: *cysteine, corrosion, green inhibitors, carbon steel.*

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ABSTRAK

Peran gugus fungsi molekul sistein (asam 2-amino-3-merkaptopropanoat) terhadap penghambatan korosi baja karbon API 5L X65 dalam larutan NaCl 0,25 M jenuh CO₂ telah dipelajari menggunakan metode polarisasi (Tafel) dan impedansi (EIS), bersama dengan perbandingan tindakan penghambatan dengan senyawa alanin dan asam 3-merkaptopropionat. Hasil penelitian ini menunjukkan bahwa mekanisme penghambatan sistein terjadi melalui pembentukan lapisan pelindung yang tidak rata pada permukaan baja karbon. Adsorpsi molekul sistein pada permukaan baja karbon memenuhi isotherm Langmuir dan teradsorpsi melalui adsorpsi fisik. Gugus merkapto berperan dalam pembentukan film, sedangkan gugus amina menyebabkan adsorpsi film yang tidak merata pada permukaan baja karbon. Sistein tergolong inhibitor anodik dengan efisiensi penghambatan hingga 90% pada konsentrasi 0,25 mM.

Kata Kunci: *sistein, korosi, inhibitor hijau, baja karbon*

INTRODUCTION

Currently, the development of corrosion inhibitors is oriented towards environmentally friendly organic compounds. In the last two decades, research in the field of corrosion inhibitors has focused on the use of organic molecules which have availability, low cost, non-toxic, and effective to diminish the corrosion rate [1,2]. These compounds include plants extract [3–7], algae [8–12], amino acids and its derivatives [13–16], and they have been examined as corrosion inhibitors for various metals, such as steel [7,10,15], tin [5,17], copper

[18,19], aluminum [20–22], and alloy [22,23], in acidic or neutral media.

The utilization of organic compounds as corrosion inhibitors requires a comprehension of the mechanisms that related to the molecular structure and its functional groups [24–26]. The corrosion inhibition mechanism is by means of the formation of a film consisting of a layer of adsorbed molecules on the metal surface [27]. Corrosion inhibitors that can form a film on the metal surfaces include (1) amine compounds, (2) heterocyclic nitrogenous compounds, and (3) organic compounds containing mercapto, amine, and/or

thiocarbamide groups [24,28-32]. The inhibitory ability of carbon compounds is based on the strength of the interaction and adsorption towards the metal surfaces.

In this work, cysteine (Cys) compound containing amine, mercapto, and carboxyl groups was studied as corrosion inhibitors. Cys is relatively inexpensive, non-toxic and easy to manufacture in high purity. Cys was examined as a corrosion inhibitor for carbon steel in a 0.25 M NaCl solution saturated with CO₂, a condition similar to that of a petroleum production well [33,34]. Potentiodynamic polarization (Tafel) and electrochemical impedance spectroscopy (EIS) methods were used in this investigation.

The role of functional groups in Cys molecules in the corrosion inhibition process of carbon steel was studied using 3-mercaptopropanoic acid (MPA) and alanine (Ala) as comparison molecules. MPA can be considered as a Cys molecule sine an amine group, whilst Ala as a Cys molecule sine a mercapto group. Namely, the role of the mercapto group in the Cys molecule could be studied based on the corrosion inhibitory activity of MPA, whereas the role of the amine in the Cys molecule was studied based on the corrosion inhibitory activity of Ala. The molecular structure of these compounds are shown in Figure 1.

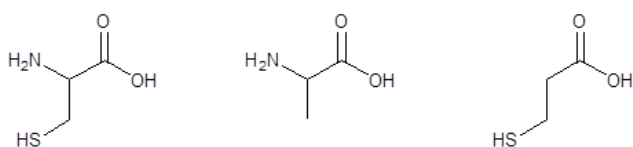


Figure 1. Molecular structure of (a) cysteine, Cys; (b) alanine, Ala; (c) 3-mercaptopropanoic acid, MPA

METHODS

Sample Preparation

The measurements were performed in an electrochemical cell with three conventional electrodes, i.e. the working electrode, the reference electrode, and the counter electrode. The working electrode uses API 5L X65 carbon steel with a composition as shown in Table 1.

The working electrode rod was coated with epoxy resin to acquire an exposure area of 1.5 cm². Before use, the surface of the electrode is polished with sandpaper up to 1200 grade, cleaned with acetone, washed with water and dried. The saturated calomel electrode (SCE) was used as the reference electrode, and the platinum electrode was used as the counter electrode [35]. All measurements were conducted in CO₂-saturated 0.25 M NaCl solutions.

Table 1. Chemical composition of API 5L X65 carbon steel

Element	%(w/w)	Element	%(w/w)
Carbon (C)	0.0737	Chrome (Cr)	0.0224
Silicon (Si)	0.2882	Copper (Cu)	0.0051
Sulphur (S)	0.0068	Tungsten (W)	0.0030
Phosphorus (P)	0.0153	Aluminium (Al)	0.0282
Manganese (Mn)	1.5353	Iron (Fe)	rest
Nickel (Ni)	0.0129		

Potentiodynamic polarization and impedance measurement

The potentiodynamic polarization and impedance measurements were performed using an electrochemical workstation (Tacussel-Radiometer PGZ 301) and controlled with Tacussel corrosion analysis software (Voltmaster 4). Prior to the potentiodynamic polarization or electrochemical impedance measurements, the working electrode was immersed in the test solution for 30 minutes for stabilization of the open circuit potential (OCP).

In the potentiodynamic polarization measurement, anodic and cathodic polarization curves were recorded by a constant sweep rate of 0.5 mVs⁻¹, potential range ± 75 mV with respect to OCP [36]. The corrosion rate (CR) was determined by the Tafel extrapolation method and fitting the linear part of the curve, and the calculated using the following equation [37]:

$$CR = 3.27 \times 10^{-3} \frac{i_{corr} EW}{\rho}$$

where CR is the corrosion rate (mm per year), *i*_{corr} is the corrosion current density (mA/cm²), EW is the equivalent weight of the corroding species (g) and ρ is the density of the corroding material (g/cm³).

Impedance spectra were obtained in the frequency range 50 kHz to 10 mHz with ten points per decade at the corrosion potential after 30 minutes of immersion. A sine wave with an amplitude of 10 mV was used to perturb the system, and the DC potential is applied with respect to the OCP [38]. The impedance diagrams are given in the Nyquist representation.

For the purposes of morphological study, the surface features of carbon steel (0.8×0.01 × 0.8×0.01 × 0.2×0.01 cm) were analysis after exposure to CO₂-saturated 0.25 M NaCl solutions after 12 hours with and without the addition of inhibitor.

RESULT AND DISCUSSION

Mechanism of cysteine inhibition

Potentiodynamic polarization analysis by the Tafel technique as shown in Figure 2 was used to derive the corrosion parameters, such as corrosion potential (*E*_{corr}), cathodic (β_c) and anodic (β_a) Tafel constants, and corrosion current density (*i*_{corr}). These corrosion parameters are presented in Table 2.

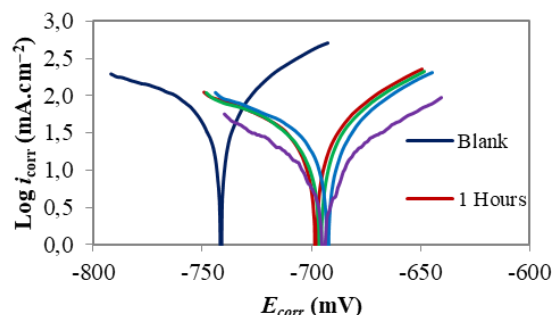


Figure 2. Potentiodynamic polarization curve for API 5L X65 carbon steel in testing solution containing Cys 0.10 mM at various exposure times

At room temperature, the addition of 0.10 mM Cys shifted E_{corr} to a more positive direction (anodic), and its value remained relatively constant with increasing exposure time. This potential shift is accounted by the presence of a functional group in the cysteine molecule which can polarize the carbon steel surface in the anodic direction, specifically a functional group that is negatively charged (carboxyl group) or partially negatively charged (mercapto group).

Table 2. The influence of exposure duration on corrosion parameters of API 5L X65 carbon steel in a testing solution containing Cys 0.10 mM at 300K

Time (hours)	E_{corr} (mV)	β_a (mV)	β_c (mV)	i_{corr} ($\mu A/cm^2$)	CR (mmpy)
blank	-742.1	82.7	-158.9	146.423	1.713
1	-698.4	58.5	-112.5	35.266	0.432
3	-694.8	55.3	-107.5	32.284	0.378
6	-692.1	54.7	-91.1	25.952	0.303
12	-694.4	50.9	-83.6	15.801	0.185

Moreover, the addition of Cys also reduces i_{corr} that leads a decrease in the corrosion rate (CR) of carbon steel. If the decrease in CR is associated with the anodic (β_a) and the cathodic (β_c) Tafel constant, it can be expressed that the addition of Cys into the medium is able to suppress the corrosion process in both anodic and cathodic. However, since the carbon steel surface is polarized in the anodic direction, Cys is more dominant in inhibiting the anodic corrosion process. In this case, Cys plays a more important role in inhibiting the formation of Fe^{2+} ions on the carbon steel surface by decreasing the corrosion current density [23,39-41], rather than as the scavenger of H^+ ions resulting from CO_2 ionization in the medium [29] according to chemical equation: $CO_2(aq) + H_2O(l) \rightarrow H^+(aq) + HCO_3^-(aq)$.

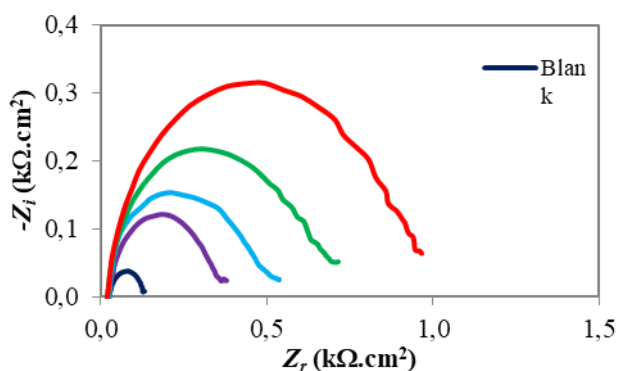


Figure 3. Nyquist plots of API 5L X65 carbon steel in testing solution containing Cys 0.10 mM at various exposure times

The results of the impedance measurement towards API 5L X65 carbon steel in the testing solution are expressed in a Nyquist diagrams as shown in Figure 3. These diagrams are a plot of imaginary impedance [$Z_i(\omega)$] as a function of real impedance [$Z_r(\omega)$], from $\omega \rightarrow 0$ to $\omega \rightarrow \infty$ [35,42,43]. The analysis of the impedance spectra curve give the values of solution resistance (RS), charge transfer resistance (RCT), and

electrical double layer capacitance (CDL), that are presented in Table 3.

Table 3. The influence of exposure duration on the impedance and the electrical double layer capacitance of carbon steel in a testing solution containing 0.10 mM Cys

Time (hours)	R_s ($\Omega.cm^2$)	R_{CT} ($\Omega.cm^2$)	C_{DL} ($\mu F.cm^{-2}$)
blank	25.79	106.40	373.8
1	23.90	347.10	144.8
3	22.20	469.60	156.9
6	21.14	682.30	186.6
12	20.57	950.90	264.4

As shown in Table 3, the addition of Cys to the testing solution relatively did not change the resistance of the solution (RS). This indicates that the added Cys is in the molecular form. However, the addition of Cys could increase the charge transfer resistance (RCT) on the carbon steel surface. This evidence is by reason of the Cys molecules cover the surface of the carbon steel to form an insulating layer, therefore the charge transfer that controls the corrosion rate of carbon steel at the interface is inhibited [19,40,44,45].

The CDL values varies inversely with the thickness of the insulating layer covering the carbon steel surface. The addition of Cys to the testing solution lowers the value of CDL, this signifies that an insulating layers have formed on the surface of the carbon steel with a particular thickness [43,45]. As the duration of exposure accrues, the CDL values increase due to the porosity of the insulator layers which could escalate the local dielectric constant [46,47].

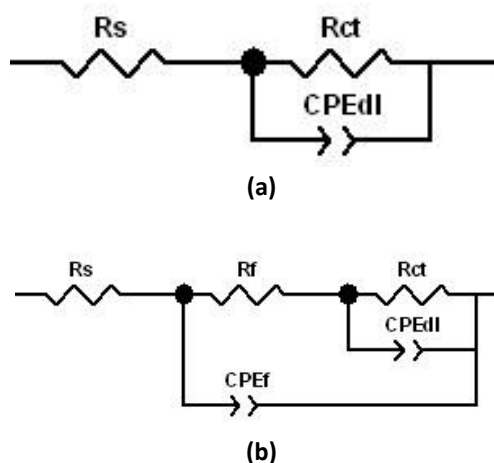


Figure 4. Equivalent electrical circuit models for carbon steel in a CO2-saturated 0.25 M NaCl solution (a) in the absence and (b) presence of Cys

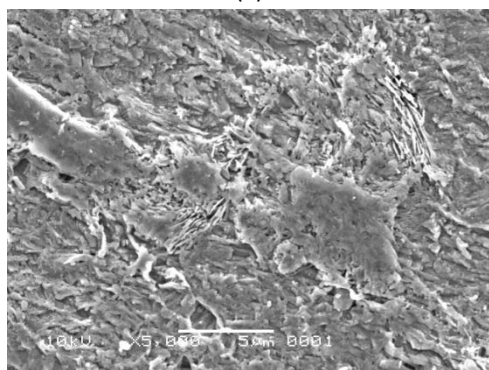
Electrical properties at the interface could be studied thru simulating an equivalent electrical circuit model by fitting the impedance spectra curve from the EIS measurement results to the impedance spectra curve from the simulation results. Based on the simulation proceeds, the equivalent electrical circuit models for carbon steel in the testing solution without

and with the addition of Cys are shown in Figures 4a and 4b, respectively.

The model of equivalent electric circuit in Figure 4a represents the electrical phenomena at the interface due to the interaction of the carbon steel surface and the solution. This circuit model (Fig. 4a) describes the condition of carbon steel as immersed in a solution as a protective layer on its surface, this model also known as the Randles circuit model [35,43,48]. Whereas the equivalent electrical circuit model in Figure 4b denotes that the corrosion rate of carbon steel is controlled by charge transfer kinetics and is inhibited by an uneven and porous protective layer on the surface of carbon steel [40,43,48], so that ions in solution can still penetrate it. The existence of this porosity is indicated by a series of CPEf that is directly connected to the surface of the carbon steel. The unevenness of the protective layer was proven by analyzing the surface morphology of the carbon steel using a scanning electron microscope (SEM), as shown in Figure 5.



(a)



(b)

Figure 5. SEM image of carbon steel surface after being immersed in CO₂-saturated 0.25 M NaCl for 12 hours with 10000 \times magnification (a) in the absence and (b) presence of Cys 0.10 mM

The adsorption properties of Cys molecules on the carbon steel surface could be determined from the value of adsorption free energy (ΔG_{ads}) thru the Temkin or Langmuir adsorption isotherm at 300K [42,48]. The linear equations of the two isotherms are as follows [49,50]:

$$\text{Langmuir } \frac{C_{inh}}{\theta} = C_{inh} + \frac{1}{K} \quad (2)$$

$$\text{Temkin } \log C_{inh} = -\frac{2a}{2,303}\theta - \log K \quad (3)$$

where C_{inh} is the concentration of Cys added to the testing solution, θ is the fraction of surface coverage of the carbon steel by the adsorbed Cys molecules, and K is the adsorption-desorption equilibrium constant. The value of K is related to the value of ΔG_{ads} by the equation:

$$K = \frac{1}{C_s} \exp\left(-\frac{\Delta G_{ads}}{RT}\right) \quad (4)$$

where C_s represents the molar concentration of water and ΔG_{ads} is the change in the free energy of adsorption.

The carbon steel surface coverage fraction (θ) by Cys molecules is acquired from the value of the charge transfer resistance (RCT) via the equation:

$$\theta = \frac{R_{CT(inh)} - R_{CT(0)}}{R_{CT(inh)}} \quad (5)$$

where $R_{CT(0)}$ and $R_{CT(inh)}$ are the charge transfer resistance in the absence and presence of Cys, respectively. The surface coverage fractions (θ) at various Cys concentration are presented in Table 4. The Langmuir and Temkin isotherm plot is shown in Figure 6.

Table 4. The surface coverage fraction at various concentrations of Cys based on the value of charge transfer resistance measured by EIS

C_{inh} (mM)	R_{CT} ($\Omega \cdot \text{cm}^2$)	θ	$\log C_{inh}$	C_{inh}/θ
0.00	54.5	—	—	—
0.05	199.4	0.7265	-1.301	0.688
0.10	264.3	0.7936	-1.000	0.125
0.15	345.8	0.8423	-0.824	0.177
0.20	435.7	0.8748	-0.699	0.231
0.25	467.8	0.8834	-0.602	0.284
0.30	493.8	0.8896	-0.523	0.338

Based on the linearity of the adsorption isotherm in Figure 6, it can be seen that the adsorption of Cys on the carbon steel surface obeys the Langmuir isotherm. The adsorption free energy (ΔG_{ads}) value obtained from the Langmuir isotherm was -20.276 kJ/mol. Accordingly, the adsorption of Cys on the API 5L X65 carbon steel surface is dominated by physical adsorption [49-51]. Moreover, empirical evidence that Cys molecules have been adsorbed on the carbon steel surface could be seen from the Energy Dispersive X-Ray Analysis (EDAX) spectra as shown in Figure 7.

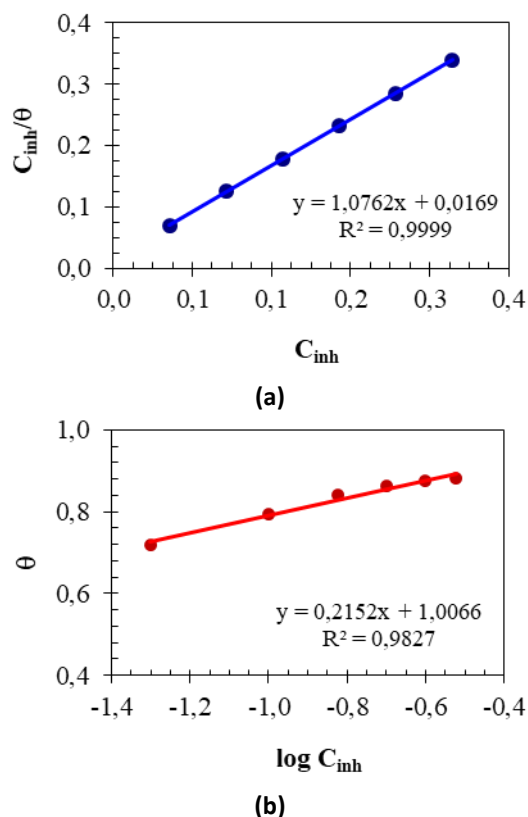


Figure 6. The adsorption isotherm of Cys on carbon steel surface in CO₂-saturated 0.25 M NaCl solution (a) Langmuir isotherm and (b) Temkin isotherm

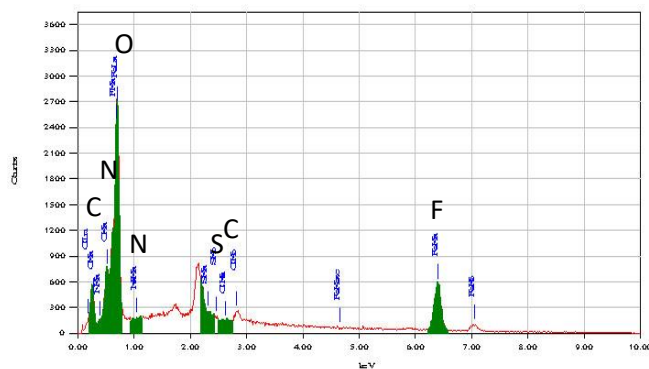


Figure 7. Energy dispersive X-ray spectrogram of carbon steel exposed in CO₂-saturated 0.25 M NaCl in the presence of 0.1 mM Cys for 12 hours

The role of cystein functional groups in the corrosion inhibition process

The addition of Cys, MPA, and Ala separately to the testing solution at room temperature shifted the E_{corr} of carbon steel to a significantly more positive direction, save for Ala which gave a very small shift, as shown in Figure 8 and Table 5. The E_{corr} shifts for the testing solution containing Cys and MPA are relatively similar, these indicate that the carbon steel surface is polarized by the same functional groups. These phenomena are also confirmed by a decrease in the corrosion rate. The decrease in the corrosion rate of carbon steel in a testing solution containing 0.10 mM MPA and 0.10 mM Cys are very

significant with an inhibition efficiency (IE) value reach 90% [34]. Whilst the decrease in corrosion rate was relatively small with an IE only 20% in the testing solution containing Ala 0.10 mM.

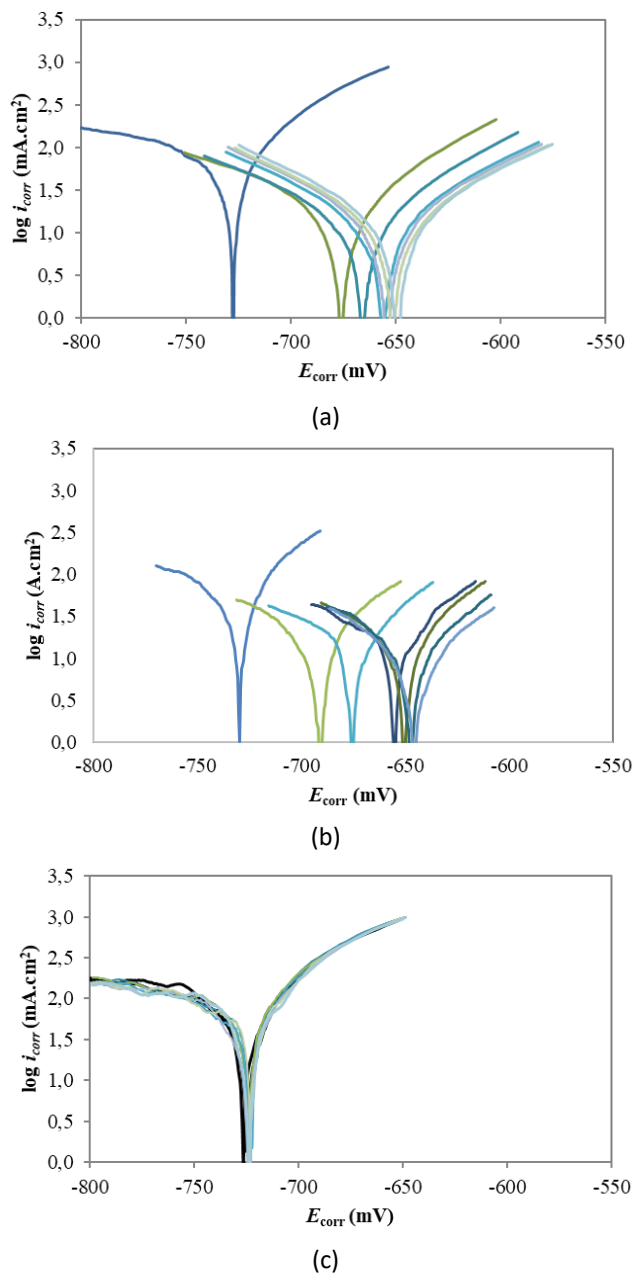


Figure 8. Potentiodynamic polarization curves for API 5L X65 in CO₂-saturated 0.25 M NaCl solution at 298 K containing (a) Cys, (b) MPA and (c) Ala.

The Cys molecule contains three protons which could be ionized in water with the values of ionization constant $pK_{-COOH} = 1.91$, $pK_{-NH_2} = 10.28$ and $pK_{-SH} = 8.14$ [52], and the degree of ionization depends on the pH of the solution. At the isoelectric point, $pH = 5.07$, the Cys molecules form the zwitter ions which are entirely neutral in charge and form the stable ions in the pH range of 1.91-8.14. The testing solution has a pH of 4.75 ± 0.05 due to dissolved CO₂, therefore the Cys molecules are stable in they ionic form with a structure as shown in Figure 9.

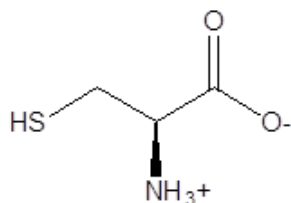


Figure 9. The molecular structure of Cys in the form of zwitter ions

The polarization of the carbon steel surface towards a more positive direction due to the amine group is very slight, because this functional group is in a protonated state, $-NH_3^+$, in solution. Therefore, the polarization of carbon steel surface in a more positive direction is due to the $-SH$ or $-COO^-$ groups. Cys and MPA polarize the carbon steel surface in a more positive direction, indicating that the two compounds are more negatively charged. However, amongst the two negatively charged functional groups that play a role in polarizing the carbon steel surface is the $-SH$ group. This is based on the fact that Ala also contains a carboxyl group still is unable to polarize carbon steel in a significantly more positive direction. Moreover, the carboxyl group is ionic which is more soluble in water (hydrated) than the mercapto group.

The high polarity of the $-SH$ group is able to polarize the carbon steel surface in a more positive direction, this induces a relatively high partial charge difference between them, as though a capacitor. The impact of this polarization inflicts dipole-dipole interactions between the $-SH$ groups and Fe atoms to form a physically adsorbed protective layer. Hence, it can be stated that the $-SH$ group plays a role in the adsorption process, whilst the $-COO^-$ group tends to be solvated in solution, as illustrated in Figure 10.

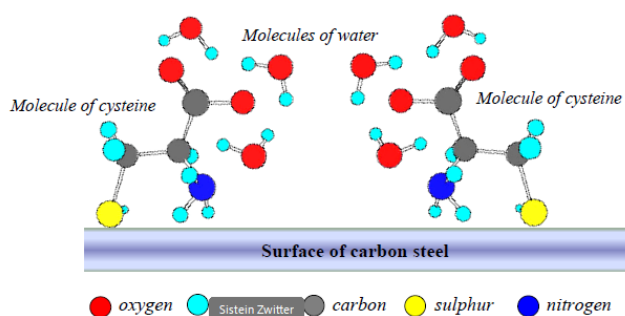


Figure 10. The model of Cys adsorption on the carbon steel surface

Based on the simulation of the equivalent electric circuit model, it is known that the equivalent electric circuit model for Ala shows the formation of an uneven and porous protective layer. Whereas the equivalent electrical circuit model for MPA shows the formation of a perfect protective layer, as shown in Figure 11 [23,34,53-55].

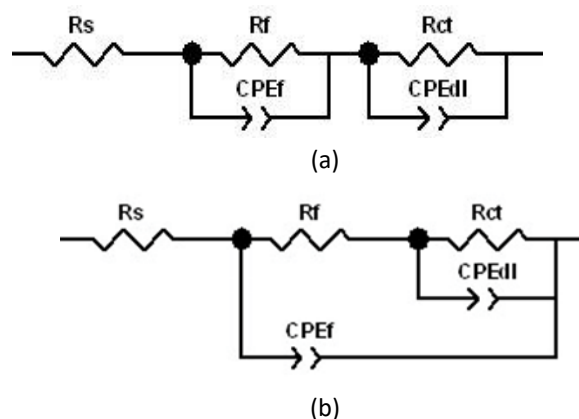


Figure 11. The equivalent electrical circuit model for carbon steel in a CO_2 -saturated 0.25 M NaCl solution containing (a) MPA and (b) Ala

The equivalent electrical circuit model for carbon steel in a solution containing Cys is similar to the model for Ala. This indicates that the imperfection of the protective layer on the carbon steel surface is caused by the presence of a small portion of the amino group which is also adsorbed on the surface of the carbon steel and inflicts a repulsion between the carboxyl groups. This repulsion is due to the non-linear structure of the Cys molecule.

CONCLUSIONS

The mechanism of cysteine inhibition on the corrosion of carbon steel in CO_2 saturated 0.25 M NaCl solution at room temperature is initiated by polarizing the carbon steel surface in a more positive direction by the partially negatively charged $-SH$ group, followed by a van der Waals interaction between the carbon steel surface and the $-SH$ group to form a physisorption protective film that obeys to the Langmuir isotherm. The protective layer formed is uneven due to the involvement of the $-NH_3^+$ group in the interaction with the carbon steel surface, which leads a repulsion between the $-COO^-$ groups. Cysteine as a corrosion inhibitor for API 5L X65 carbon steel is classified as an anodic inhibitor with an inhibition efficiency reach of 90% at a concentration of 0.25 mM.

AUTHOR CONTRIBUTION

YS conceived the presented idea and developed the theory. BA supervised the data collection and analyze the findings. GY, HSHM, and AM performed the data analysis. All authors discussed the results and contributed to the final manuscript.

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