CORROSION MONITORING OF COLD ROLLED STEEL IN HCL SOLUTIONS

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ABSTRACT

Corrosion studies for protection of cold rolled steel (CSR) in aerated stagnant 1.0 M HCl solution at 25 ^{0}C was carried out using Glycine and its derivative namely 2 – (bis (2- aminoethyl)amino) acetic acid, designated as GlyD. Corrosion rates were measured using Tafel polarization, linear polarization and impedance technique. GlyD was found to be more effective in inhibiting the acid corrosion of CRS. Tafel polarization method was validated by Electrochemical frequency modulation (EFM) and inductively coupled plasma – atomic emission spectroscopy (ICP – AES) and was in good agreement with the trend.

1.Introduction

Corrosion inhibition of steel, therefore is a matter of theoretical as well as practical of the important fields of applications being acid pickling of iron and steel, chemical cleaning and processing, ore production and oil well acidification. Because of the aggressiveness of acid solutions, inhibitors are commonly used to reduce the corrosive attack on metallic materials. Most well-known acid inhibitors are organic compounds containing nitrogen, sulfur, and oxygen atoms. However, these compounds, despite their high inhibition performance, are toxic and carcinogenic. The safety and environmental issues of corrosion inhibitors arisen in industries has always been a global concern. However, only a few non-toxic and eco-friendly compounds have been investigated as corrosion inhibitors. Amino acids are environmentally friendly compounds. In addition, amino acids are from a class of organic compounds, completely soluble in aqueous media. These properties would justify their use as corrosion inhibitors.

Tafel polarization, linear polarization (LP) and impedance techniques are applied to study the ability of glycine (Gly) and a glycine derivative, namely 2-(bis(2-aminoethyl)amino) acetic acid, abbreviated here as GlyD, as safe-inhibitors, to inhibit a cold rolled steel (CRS) corrosion in aerated stagnant 1.0 M HCl solutions. EFM and ICP-AES methods were also applied to monitor rates of corrosion and test validation of corrosion rates measured by Tafel

extrapolation method. It was also the purpose of the present work to discuss the experimental protection efficiencies of the two tested inhibitors.

2.Experimental studies

Experiments were performed on a cold rolled steel (CRS) of the following composition (wt.%): 0.14% C, 0.2% Mn, 0.025% P, 0.008% S, 0.025% Si, 0.003% Al, and bal. Fe. All solutions were freshly prepared from analytical grade chemical reagents using doubly distilled water. Each run was carried out in stagnant aerated solutions at the required temperature. Electrochemical measurements were carried out in a conventional electrochemical cell containing three compartments for working (with an exposed area of 1.0 cm^2), a platinum foil (1.0 cm^2) counter and reference electrodes. A Luggin–Haber capillary was also included in the design. The tip of the Luggin capillary is made very close to the surface of the working electrode to minimize IR drop. The reference electrode was a saturated calomel electrode (SCE) used directly in contact with the working solution. The experiments were conducted in a 150 cm^3 volume cell, open to air, at 25 ^{o}C $\pm$ 2 using a temperature control water bath.

All potential values were reported in volt (SCE). Test run was carried out in stagnant aerated 1.0 M HCl solutions without and with various concentrations (0.1–5.0 mM) of glycine (Gly) or its derivatives (GlyD) as corrosion safe-inhibitors for steel. The chemical structure of Gly and its derivative are illustrated below:

Glycine
(Gly)

2-(bis(2-aminoethyl)amino)acetic acid
(GlyD)
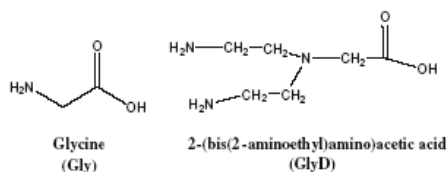
Polarization measurements were carried out starting from a cathodic potential of _0.60 V to an anodic potential of _0.35 V at a sweep rate of 0.20 mV s-1. Impedance measurements were carried out using AC signals of amplitude 5.0 mV peak to peak at the opencircuit potential in the frequency range 30 kHz to 1.0 mHz. All impedance data were fitted to appropriate equivalent circuits using the computer program EQUIVCRT [1].EFM measurements were performed with applying potential perturbation signal with an amplitude of 10 mV with two sine waves of 2 and 5 Hz. The Intermodulation spectra contain current responses assigned for harmonical and intermodulation current peaks. The larger peaks were used to calculate the corrosion current density (jcorr), the Tafel slopes (bc and ba) and the causality factors CF2 and CF3.

All electrochemical experiments were carried out using Gamry PCI300/4 Potentiostat/Galvanostat/Zra analyzer, DC105 Corrosion software, EIS300 Electrochemical Impedance Spectroscopy software, EFM140 Electrochemical Frequency Modulation software and Echem Analyst 5.21 for results plotting, graphing, data fitting and calculating.

3.Results and Discussion
3.1. Polarization measurements
3.1.1. Tafel polarization. Figs. 1a and b illustrate the cathodic and anodic polarization curves recorded for CRS electrode in aerated stagnant 1.0 M HCl solutions without and with various concentrations (0.1–5.0 mM) of Gly or GlyD at a scan rate of 0.20 mV s_1 at 25

°C. These polarization curves demonstrate, as a first sight, that in presence of either Gly or its derivative the cathodic and anodic branches of the polarization curves are shifted towards lower currents to very similar extent, probably as a consequence of the blocking effect of the adsorbed inhibitor molecules. No significant changes were observed in Ecorr values in presence of inhibitors. It seems, therefore that the two inhibitors inhibit corrosion by controlling both anodic and cathodic reactions (mixed-type inhibitors). In acidic solutions, as will be seen and fully discussed in Section 5, Gly and its derivative exist as protonated species. These protonated species adsorb on the cathodic sites of the steel, inhibiting hydrogen evolution reaction. The adsorption on anodic sites may occur through lone pair of electrons of un-protonated nitrogen atoms, which retards anodic dissolution of steel.

It is also seen, in all cases, that the cathodic branches of the polarization curves display a typical Tafel behaviour. This makes it possible, as will be seen, to make an accurate evaluation of the cathodic Tafel slope (bc) as well as corrosion currents (jcorr) by the Tafel extrapolation method. On the other hand, the anodic polarization curves presented here do not display the expected log/linear Tafel behaviour over the complete applied potential range. The curvature of the anodic branch may be attributed to the deposition of the corrosion products or impurities in the steel (e.g., Fe3C) to form a non-passive surface film [2]. In addition, a clear inflection is quite clear in the anodic branches, may be due to passivation and pitting. Other researchers also noted this inflection in the anodic domain of CRS in HCl solutions at a certain potential

designated, in their study, as the desorption potential, ca. _300 mV vs. SCE [3].

The authors demonstrated that the behaviour of the inhibitor (the selected inhibitor in their study was 6-benzylaminopurine, BAR) at potentials greater than the desorption potential could be associated to the significant dissolution of steel. This dissolution results in desorption of BAR-adsorbed film in 1.0 M HCl media [3]. In this case, desorption rate of BAR is raised more than its adsorption, since BAR had a very little influence on the anodic reaction at potentials higher than _300 mV vs. SCE However, in the present work, the presence of Gly or its derivative inhibits anodic reaction markedly, even at potentials anodic to the desorption potential, inspect again anodic domains presented in Fig. 1.

This result shows clearly the anodic inhibition influence of Gly and its derivative, besides their obvious cathodic inhibiting effect, to the HCl corrosion of steel. The existence of this inflection in the anodic domain does not result in a well-defined experimental anodic Tafel region. This undoubtedly makes it impossible to make an accurate evaluation of the anodic Tafel slopes (ba) by Tafel extrapolation [2,9]. There is, therefore an uncertainty and source error in the numerical values of (ba), and may be in values of jcorr too, calculated by the software; the reason why we did not introduce here jcorr as well as (ba) values recorded by the software. On the same basis, we can- not determine jcorr from impedance plots, since these require Tafel slopes.

For these reasons we used, as will be seen latter, EFM, a non-destructive corrosion measurement technique that can directly give values of corrosion

current without prior knowledge of Tafel slopes. Corrosion rates determined using EFM method were compared with those obtained from the Tafel extrapolation method with the aim to test its validity for corrosion rate measurements.

It has been shown that in the Tafel extrapolation method, use of both the anodic and cathodic Tafel regions is undoubtedly preferred over the use of only one Tafel region [8]. However, the corrosion rate can also be determined by Tafel extrapolation of either the cathodic or anodic polarization curve alone. If only one polarization curve alone is used, it is generally the cathodic curve which usually produces a longer and better defined Tafel region (see our cathodic polarization curves). Anodic polarization may sometimes produce concentration effects, due to passivation and dissolution, as noted above, as well as roughening of the surface which can lead to deviations from Tafel behaviour. Thus, extrapolation of the cathodic Tafel region back to zero overvoltage gives the net rate of the cathodic reaction at the corrosion potential; this is also the net rate of the anodic reaction at the corrosion potential [8]

$$j_a(\text{net experimental}) = j_a - j_c$$

where the subscripts a and c refer to the anodic and cathodic direction, respectively. Thus, the calculated anodic current density, ja, is the sum of the experimentally observed anodic current density and the extrapolated cathodic current density. The result as a representative example for such calculations, is that jcorr = 8.86 X 10_5 A cm_2. It is quite safe now to collect accurate values of the electrochemical parameters, as jcorr, Ecorr, ba and bc, in a Table like Table 1, as a function of the

inhibitor concentration. The values of the cathodic Tafel slope (bc) remain almost unchanged upon increasing Gly or GlyD concentrations; the reason why cathodic polarization curves give rise to parallel Tafel lines. These findings indicate that the hydrogen evolution reaction is activation-controlled and the addition of Gly or its derivative does not affect the mechanism of the corrosion process [9]. This means that the inhibition of the hydrogen evolution reaction by Gly or GlyD occurs by simple adsorption mode and the mechanism is the same without and with inhibitor. The action of Gly and its derivative may be related to their adsorption adsorption and formation of a barrier film on the electrode surface, protecting it against corrosion. Since the corrosion rate is directly proportional to the value of the corrosion current density, the protection efficiency (PTafel(%)), see also Table 1, was evaluated from the measured jcorr values using the well-known relationship:

$$P_{\text{Tafel}}(\%) = 100 \times \left[(j^o_{corr} - j_{corr})/j^o_{corr} \right]$$

where jo and jcorr are the corrosion current densities for uninhibited and inhibited solutions, respectively. It is apparent that the protection efficiencies of Gly and its derivative enhance with increase in their concentration. A maximum protection efficiency of about 97% was recorded for GlyD at a concentration of 5.0 mM. These results reflect the highest protection performance of GlyD compared with that of Gly itself under these conditions.

3.1.2. Linear Polarization (LP) measurements

For linear polarization (LP) measurements, a sweep from _20 to +20 mV vs. open-circuit potential at a sweep

rate of 0.20 mV s_1 was used and the polarization resistance (Rp) was measured from the slope of g vs. j curve in the vicinity of corrosion potential. Since the electrochemical theory assumes that 1/Rp is directly proportional to the corrosion rate, the protection efficiencies, PLP(%) of Gly were calculated from (Rp) values obtained from LP data at different inhibitor concentrations, using Eq. (5):

$$P_{LP}(\%) = \left\{ \left(R_P - R_P^o \right) / R_P \right\} \times 100$$

where Ro and Rp are the polarization resistance values without and with the addition of inhibitor, respectively.

The polarization resistance (Rp) values of steel in 1.0 M HCl solutions increase with increase in the concentration of the two inhibitors (Table 1). The increase in the Rp value suggests that the protection efficiency increases with the increase in the inhibitor concentration (inspect PLP(%) values presented in Table 1)

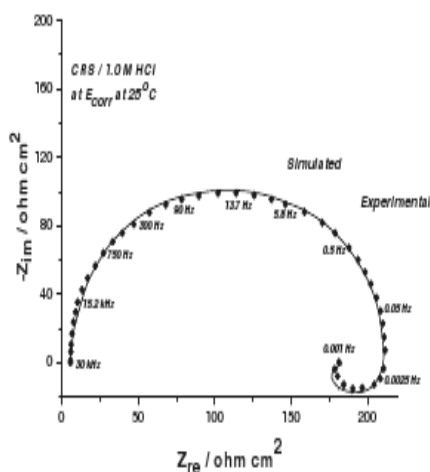### 3.2.Impedance measurements

Fig. 2. A complex-plane impedance plot obtained for CRS electrode in aerated stagnant 1.0 M HCl solution at the corrosion potential at 25 °C.

Fig. 2 presents the complex-plane impedance plot obtained for the steel electrode in 1.0 M HCl solution at the corrosion potential at 25 _C. It is seen that a high frequency (HF) depressed chargetransfer semicircle was observed followed by a well-defined inductive loop in the low-frequency (LF) regions. Similar results were obtained in our previous study [9]. Depressed semicircles are usually obtained for practical electrode/solution interface, which has been known to be associated with the roughness of electrode surface. It is well-known that the corrosion of steel in the acid media, particularly HCl, increases the roughness of the electrode surface, and therefore a more depressed semicircle results. The HF semicircle is attributed to the time constant of charge-transfer and double-layer capacitance.

This semicircle intersects the real axis to give a value of about 0.85 cm2 for the resistance of the solution (Rs) enclosed between the working electrode and the counter electrode. The LF inductive loop may be attributed to the relaxation process obtained by adsorption species as Cl_ads and Hþads on the electrode surface. However, we believe that the adsorption of Cl_ads species is preferable than the adsorption of Hþads species, as the electrode potential is positively charged at the corrosion potential [9]. This LF inductive loop may also be attributed to the redissolution of the passivated surface at low frequencies. This inductive loop still appears, even in presence of the inhibitor. These findings may indicate that that steel is still dissolved by the direct charge-transfer at the inhibitor-adsorbed steel surface. It is

essential to develop the appropriate models for the impedance which can then be used to fit the experimental data and extract the parameters which characterize the corrosion process. To determine the impedance parameters of steel in these solutions, the measured impedance data were analyzed by using the computer program EQUIVCRT [1], based upon the electric equivalent circuit presented in our previous study [9], see the fitting results collected in Table 2. A good fit (see the solid curve in Fig. 2) with the experimental impedance data (represented here by solid spheres) was obtained.

Figs. 3a and b represent, respectively, the complex-plane impedance plots recorded for steel in aerated stagnant 1.0 M HCl solutions without and with various concentrations (0.1–5.0 mM) of Gly or its derivative, GlyD. Measurements were conducted at the respective corrosion potentials at 25 _C. It is clear, for the first sight, that the shapes of the impedance plots for inhibited electrodes are not substantially different from those of uninhibited electrodes. The presence of Gly or GlyD increases the impedance but does not change other aspects of the behaviour. These findings support polarization results that the inhibitor does not alter the electrochemical reactions responsible for corrosion. It inhibits corrosion primarily through its adsorption on the metal surface. In the present work, the protection efficiency of Gly and its derivative was evaluated by Rct and Cdl. The obvious depression in the HF semicircles, even in presence of the inhibitor, particularly Gly (Fig. 3a), suggests that the protection efficiency of the inhibitor was still small. From Table 2, the Rct values of the investigated

inhibitors increase with increasing concentration. At the same time the Cdl has opposite trend at the whole concentration range. These observations clearly bring out the fact that the corrosion of steel in 1.0 M HCl is controlled by a charge-transfer process. The decrease in Cdl is due to the gradual replacement of water molecules by the adsorption of the organic molecules at metal/solution interface, resulting in a protective film formation on the steel surface, then decreasing the extent of dissolution reaction .

The values of Rct are always greater, while those of Cdl are smaller in presence of GlyD (see the data presented in Table 2), confirming the highest protection characteristics of ClyD. The systematic increase of n values with concentration of the two inhibitors may be explained by decreasing in surface heterogeneity, due to the of the inhibitor on the most active adsorption sites. The value of n is always higher, at any given concentration, in presence of GlyD. This finding, in consistence with theoretical study (as will be seen), may again reflect the higher adsorption affinity of GlyD, and hence its high protection performance, compared to Gly itself. The protection efficiency, PZ(%), obtained from impedance measurements, see also Table 2, was estimated from the measured charge-transfer resistance, Rct, values using the relation:

$$P_Z(\%) = \left\{ (R_{ct} - R_{ct}^o)/R_{ct} \right\} \times 100$$

where Ro ct and Rct are transfer resistance values in the absence and presence of the inhibitor, respectively. It is apparent that the protection efficiencies of Gly and GlyD increase with increase in their concentrations.

Here again, a maximum protection efficiency of about 97% was recorded for GlyD at a concentration of 5.0 mM.

Table 2
Electrochemical parameters, together with protection efficiencies, P(%), associated with impedance measurements recorded for CRS in 1.0 M HCl solutions without and with various concentrations of Gly or GlyD at 25 °C.

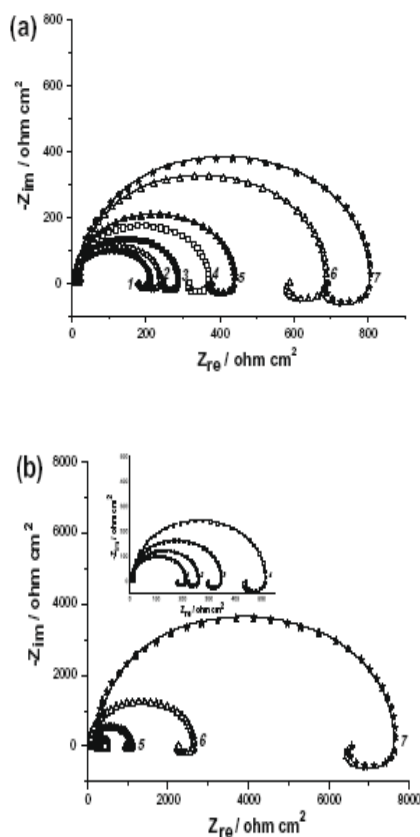| Inhibitor type	[Inhib] (mM)	R_s (Ω cm²)	Q		R_{ct} (Ω cm²)	R_L (Ω cm²)	L (H)	C_{dl} (µF cm⁻²)	P_Z (%)
			Y_0 (µF cm⁻²)	n					
Gly	Blank	5.48	148.15	0.81	182	31	213	64	0.00
	0.1	6.53	131.48	0.81	206	34	215.2	56.8	11.67
	0.2	7.76	104.89	0.82	248	40	235.8	47.36	26.55
	0.5	9.86	79.34	0.83	319	48	244	37.44	43
	1.0	11.78	59.28	0.85	378	56	267	30.56	51.84
	2.0	18.61	34.45	0.86	592	89	275.2	18.56	69.25
	5.0	2.77	28.41	0.87	695	102	290	16	73.82
GlyD	Blank	5.48	148.15	0.81	182	31	213	64	0.00
	0.1	7.00	111.21	0.83	223	37	223.4	52.48	18.22
	0.2	9.35	73.25	0.85	298	45	242	37.76	39
	0.5	13.81	46.33	0.86	443	65	251	24.96	58.95
	1.0	29.82	20.19	0.86	958	143	282	10.88	81
	2.0	71.08	9.36	0.89	2275	405	317	5.76	92
	5.0	205.82	1.82	0.92	6594	950	435	1.28	97.24

Fig. 3. Complex-plane impedance plots recorded for CRS electrode in aerated stagnant 1.0 M HCl solutions without and with various concentrations (0.1–5.0 mM) of (a) Gly and (b) its derivative, GlyD at the respective corrosion potentials at 25 °C.

These results again confirm previous findings that GlyD was better inhibitor than Gly under these conditions, see more details in Section 5. It is worth noting from Tables 1 and 2 that the protection efficiencies obtained from impedance measurements are comparableand run parallel with those obtained from Tafel polarization and LP measurements.

3.3. Monitoring of corrosion rates

Monitoring of corrosion rates in aqueous systems is critical to extending equipment life. By monitoring corrosion rates, fact based decisions can be made on the success or failure of corrosion inhibitors. Consistent corrosion protection is vital to prevent failure of metal surfaces. Corrosion rate monitoring will not only provide information on the overall success or failure of any corrosion prevention, it will also provide information on the impact of short term problems within the investigated system.

At present, weight loss measurement is the mostly employed method to acquire the corrosion rate data for metal coupons at natural environmental corrosion test stations in many countries. However, it is time-consuming, which makes the corrosion rate obtained only a long-term average. Hence few details about the corrosion process during the experimental period are revealed. Compared to weight loss method, electrochemical techniques can obtain the instantaneous corrosion rate,

implement in situ measurement, and provide plenty of information. Thus, they are expected to be applied to detect and monitor corrosion at the marine corrosion test stations. Several electrochemical techniques are available to determine corrosion rate, such as the linear polarization resistance (LPR) technique,

The LPR and EIS techniques require B value to calculate corrosion rate from polarization resistance Rp according to the equation jcorr = B/Rp. And Tafel extrapolation measurement, despite of its application here to evaluate corrosion rates, is time-consuming and will damage the electrode surface due to the polarization over a wide potential range. Compared with these three electrochemical techniques, EFM technique can quickly determine the corrosion current value without prior knowledge of Tafel slopes, and with only a small polarizing signal. These advantages of EFM technique make it an ideal candidate for online corrosion monitoring [10]; read the following section.

3.3.1. Electrochemical frequency modulation method.

The electrochemical frequency modulation technique (EFM), featuring of obtaining the Tafel slopes directly, small polarization and short measuring time, offers a novel way for electrochemical corrosion monitoring. It is generally accepted that in most cases, the corrosion rates determined with the EFM technique are much higher than the values determined with other techniques exhibiting low corrosion rates [10]. Kus and Mansfeld [10] reported that this result is mainly attributed to the fact that for systems with low corrosion rates, as Cu/NaCl and Al/NaCl, the modulation frequencies that are used in the EFM technique are in the capacitive region of the impedance spectra. The EFM approach should be mostly limited to those corrosion systems with fairly high corrosion rate, such as mild steel or iron in acidic environment. Results of the present work showed, as will be seen, good agreement of corrosion rates obtained with the EFM, Tafel extrapolation method as the steel/HCl system possesses high corrosion rates.

The EFM intermodulation spectra (spectra of current response as a function of frequency) were constructed for steel in aerated stagnant 1.0 M HCl solutions without and with various concentrations of the two tested inhibitors at 25 _C, data not included here. The obtained data were analyzed, and the protection efficiencies, PEFM(%), of the two tested inhibitors were calculated at different concentration using equations presented in our previous study [5]. The calculated electrochemical parameters (jcorr, bc, ba, CF2, CF3), together with PEFM(%) are given in Table 3. Inspections of these data infer that the values of causality factors obtained under different experimental conditions are approximately equal the theoretical values (2 and 3) indicating that the measured data are of high quality . EFM data presented in Table 3 showed again that introducing increasing concentrations of Gly or GlyD to HCl solutions decreases the corrosion current density (jcorr), which is in a good agreement with jcorr obtained from Tafel extrapolation method (inspect Tables 1 and 3), indicating that these inhibitors inhibit the acid corrosion of iron through adsorption. The calculated protection efficiencies of the tested

inhibitors enhance with their concentration.

Table 3

Electrochemical kinetic parameters and protection efficiencies, P(%), obtained using EFM technique, recorded for CRS in 1.0 M HCl solutions without and with various concentrations of Gly or GlyD at 25 °C.

Inhibitor type	[Inhib] (mM)	β_a (V dec^{-1})	$-\beta_c$ (V dec^{-1})	$(J_{corr}) \times 10^3$ (A cm^{-2})	P_{EFM} (%)	CF2	CF3	P_{ICP} (%)
Gly	Blank	0.08	0.100	9.35	0.00	1.92	3.02	0.00
	0.1	0.06	0.102	8.33	10.89	1.88	3.05	11.05
	0.2	0.07	0.095	7.05	24.55	1.91	3.11	25.10
	0.5	0.08	0.092	5.42	42.00	2.05	2.88	43.00
	1.0	0.07	0.093	4.54	51.48	2.11	2.90	52.01
	2.0	0.06	0.097	3.09	67.00	2.05	2.95	66.50
	5.0	0.09	0.098	2.42	74.12	1.95	2.92	73.95
GlyD	Blank	0.08	0.105	9.35	0.00	1.93	2.91	0.00
	0.1	0.08	0.091	7.83	16.24	1.89	3.11	17.12
	0.2	0.05	0.089	5.98	36.00	1.90	3.07	37.05
	0.5	0.07	0.097	3.51	62.43	1.85	2.88	61.88
	1.0	0.06	0.092	2.10	77.50	1.82	2.89	78.15
	2.0	0.08	0.095	1.03	88.95	1.95	2.93	87.96
	5.0	0.05	0.105	0.39	95.88	1.97	2.91	96.25

6. Conclusion

The effect of glycine (Gly) and a one of its derivatives, namely 2- (bis(2-aminoethyl)amino) acetic acid, abbreviated here as GlyD, was studied as safe-inhibitors for HCl corrosion of cold rolled steel (CRS) in the concentration range of 0.1–5.0 mM at 25 _C. In the present study, electrochemical methods including Tafel polarization, linear polarization, EFM and EIS were used to elucidate the adsorption of these two inhibitors onto the steel surface. Also a supplementary experiment like ICP, chemical method of analysis of the dissolved metal cations was carried out to confirm the electrochemical results. EFM and ICP methods were also applied to confirm validation of rates of corrosion measured by Tafel extrapolation method. Gly and its selected derivative revealed good inhibitory effects against CRS corrosion in aerated stagnant HCl solutions. Protection efficiencies are related to

concentration and chemical structure of the two tested amino acids. The protection efficiencies increased with increasing inhibitors concentration. GlyD caused significant inhibition more than Gly itself. The high inhibiting effect of GlyD compared with Gly was attributed to the presence of an extra NH link in the structure of the former. All the data obtained from the different methods, including those obtained from EFM technique and ICP chemical method of analysis, are in good agreement and in similar trends. Based on these results, the electrochemical frequency modulation (EFM) technique and ICP method appear valid for monitoring corrosion rates of CRS in these solutions.

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