Corrosion inhibition of lysine as basic amino acid on 316L stainless steel in 0.5 M H_2SO_4 solution

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Abstract: The corrosion inhibition of 316 L stainless steel in 0.5 M H_2SO_4 by lysine was investigated using open-circuit potential measurements, potentiodynamic polarization measurements and scanning electron microscopy (SEM) techniques. The open circuit potentials were measured in the absence and presence of different concentrations of lysine. It was found that the open circuit potential becomes more positive with increasinf the concentration of lysine. Potentiodymanic polarization measurements showed that the presence of lysine in acidic solution effects mainly the cathodic process and decreases the corrosion current to a great extent and shifts the corrosion potential towards more negative values. Results revealed clearly that lysine is a good cathodic type inhibitor for 316L stainless steel in 0.5 M H_2SO_4. The maximum inhibition efficiency of lysine was achieved at (7×10^{-2} M). Analyses of the surface by SEM confirm these results.
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1. Introduction:

Stainless steel have found very wide applications both in modern chemical industries and other places [1]. Since aggressive acid solutions are widely used for industrial purposes. The use of organic inhibitors in acidic solutions is very common, particularly in view of the high corrosion rate [2-9]. Amino acids are attractive as corrosion inhibitors because they are nontoxic, relatively easy to produce with high purity at low cost, and are soluble in aqueous media. A number of studies involving amino acids and their derivatives on the corrosion inhibition of iron and its alloys has been carried out [10, 11]. Most of the natural amino acids are the alpha amino acids which contain carboxyl and amino groups bonded to the same carbon atom. It was shown that the inhibition action of some organic compounds is based on adsorption phenomenon [12].

The object of this study is to investigate the inhibition effect of lysine on 316L stainless steel in acidic media.

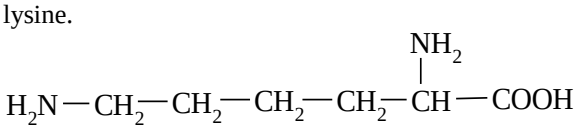
2- Experimental

The analysis of the 316L stainless steel electrode is given in Table (1).

Table (1): The chemical composition of 316L stainless steel electrode (Wt %)

Element	Si	Cr	Ni	Mo	Mn	Fe
Weight %	0.56	17.28	10.57	2.62	1.14	67.83

Circular electrode with working surface area of 1.76 Cm^2 were used. Experiments were carried out in 0.5 M H_2SO_4 solutions in absence and presence of different concentrations ($5 \times 10^{-3} - 7 \times 10^{-2}$ M) of lysine.



Diamino monocarboxylic acid (Basic amino acid)
α, ε-diamino caproic acid (lysine).

All aerated test solutions were prepared from distilled water at room temperature (25 ± 1°C) and analar reagent chemicals. Freshly polished electrodes were used for each run. Platinum electrode and standard calomel electrode (SCE) were used as counter and reference electrodes. The solution volume was fixed at 100 ml in all experiments. The open circuit potentials of the metal immersed in the test solutions were mortared using the electronic multimeter (type ES cord-EDM – 2116). The polarization measurements were run on a computerized potentiostat (Radiometer model volta Lab 40) and Volta Master 4 software. Potential scan rate in all experiments was 2 mV/s. The morphology of stainless steel surface before and after immersion in the test solutions was examined by scanning electron microscope (JEOL-JSM- 5500 LV).

3- Results and Discussion

3.1. Open-circuit potentials measurements

Open circuit potentials (OCP) were measured in the absence and presence of different concentrations (5×10^{-3}- 7×10^{-2} M) of lysine in 0.5 M H_2SO_4.

Fig. 1 represents typical curves of OCP variation with time for blank acid and inhibited solutions. Steady state potential is shifted either in the positive direction in the presence of lysine. The OCP shift in the noble direction, suggests the formation of a passive film that acts as a barrier for metal dissolution and reduces the corrosion rate by reducing the driving force of the cathodic reaction and increasing the thickness of more stable complex compound (Fe-lysine).

On introduction of lysine into the acid solution, the potential shift and attainment of a stable OCP become more noble values than those observed in the blank acid. This can be attributed to the formation of a protective layer of lysine on the stainless steel surface.

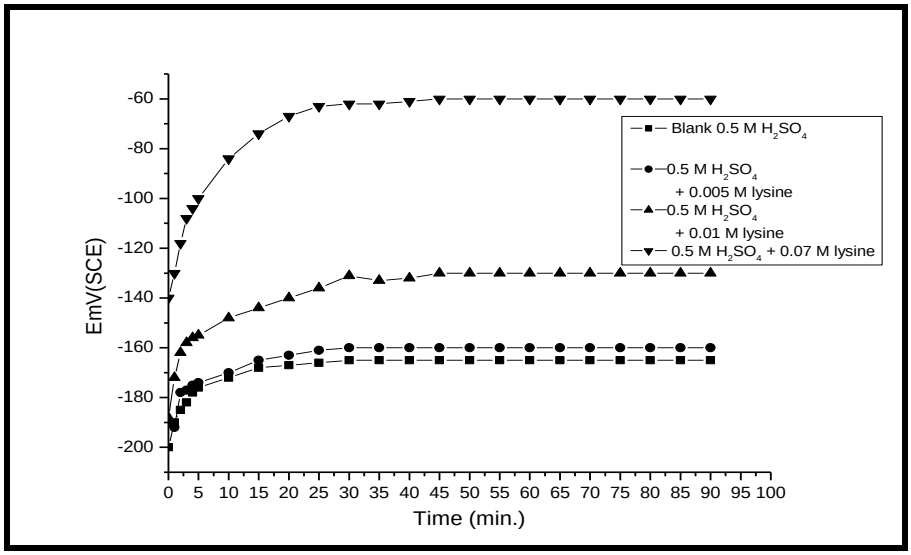
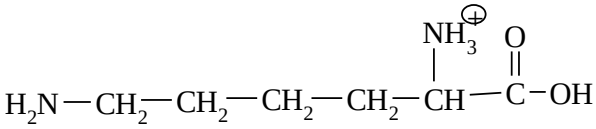


Fig. 1. Variation of the open circuit potential of 316 L stainless steel with time in 0.5 M H_2SO_4 containing different concentrations of lysine.

3.2- Liner Polarization

Fig. 2 shows the effect of lysine concentration on the polarization curves of 316 L stainless steel electrode. Corrosion parameters in the absence and presence of inhibitor obtained from curves are given in Table 2. Generally with increasing inhibitor concentration, the corrosion current density and corrosion rate decrease and polarization resistance increases (Table 2). From the results, it is found that, with increasing inhibitor concentration, $E_{corr.}$ shifts to more negative values are observed and it indicates that these inhibitors have been adsorbed to cathodic areas and act as cathodic inhibitor. Thus, the amino acid presents in its protonated form in acidic solution. Such protonated form is expected to be highly attracted to the cathodic sites on the metal surface [13].



Protonated form

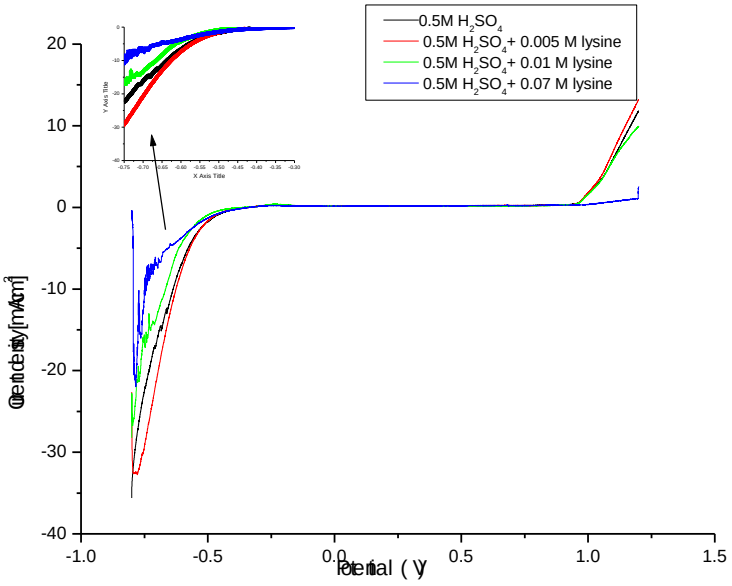
The following equation was used to the calculated inhibition efficiency (IE) from polarization measurements[14]:

$$IE = \left(1 - \frac{i}{i_o}\right) x\ 100$$

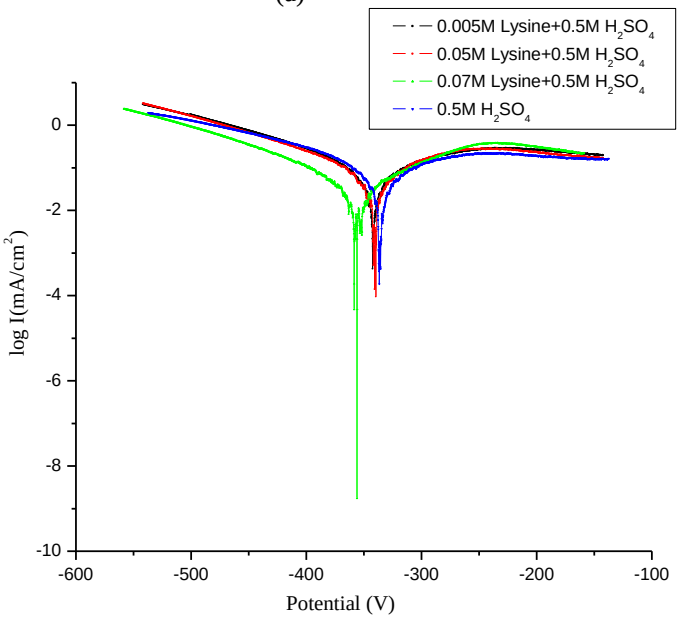
Where i and i_o are the corrosion current densities obtained by extrapolation of the cathodic and anodic Tafel lines in inhibited and uninhibited solutions, respectively.

Table (2): Corrosion parameters, and inhibition efficiency IE for 316L stainless steel in 0.5 M H_2SO_4 solution in the presence of different concentrations of lysine.

Conc. M	$E_{corr.}$(mV)	$I_{Corr.}$ mA/cm^2	Tafel slope		R_p Ωcm^2	Corrosion rate(mm/y)	IE%
			B_a	B_c			
Blank	-336.4	0.1300	160.8	-163.9	-208.38	1.520	-
5 x 10^{-3}	-341.8	0.1158	138.9	-135.6	-108.59	1.354	10.9
1 x 10^{-2}	-342.2	0.0904	114.5	-126.0	30.86	1.057	30.46
7 x 10^{-2}	-356.3	0.0558	102.8	-119.1	100.83	0.6521	57.07



(a)



(b)

Fig.2. Cathodic and anodic polarization curves for the effect of different concentrations of lysine on the potentiodynamic behaviour of 316L stainless steel in 0.5 M H_2SO_4 solution.

The inhibition efficiency increases as the inhibitior concentration increases and reaches maximum values of 57.07% at 7 x 10^{-2} M. Generally with increasing inhibitor concentration, the corrosion current density and corrosion rate decrease as shown in Fig. 3 (a and b).

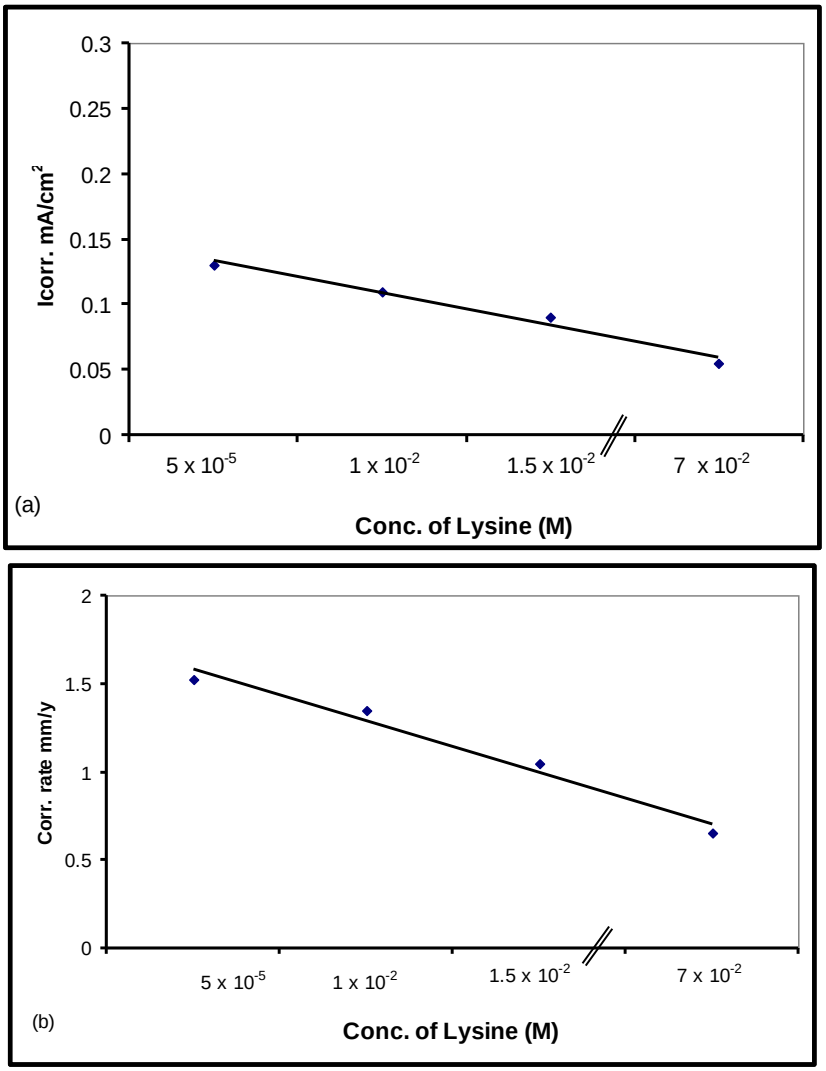


Fig. 3. Effect of lysine concentration on $I_{corr.}$(a), and on corrosion rate (b) of 316L stainless steel electrode in 0.5 M H_2SO_4 solution.

It is clear from the potentiodynamic polarization experiments that, the presence of lysine decreases the corrosion rate, i.e. the value of I_{corr} decreases. Particularly, the cathodic reaction is inhibited to larger extent than the anodic reaction. Since the transfer of oxygen from the bulk solution to the stainless steel/solution interface will strongly affect the rate of oxygen reduction, it can be inferred that the adsorbed layer behaves as a cathodic inhibitor to 316L stainless steel corrosion by retarding the transfer of O_2 to the cathodic sites of the 316L stainless steel surface.

The cathodic peaks observed at -750 mV, which increase in number by increasing the concentration of lysine.

3-3- The inhibition mechanism

The adsorption mechanism for a given inhibitor depends on such factors, as the nature of metal corrosion medium, the pH and the concentration of the inhibitor as well as the functional groups present in its molecule [15]. The corrosion inhibition process is based on the adsorption of the amino acid molecules on the active sites and/or deposition of the corrosion products on the alloy surface [16,17]. Thus it is possible to suggest that at low concentration, the amount of lysine in the solution was insufficient to form a compact complex with the metal ions, so that the resulting adsorbed intermediate was readily soluble in the acidic environment. As the concentration is increased, more lysine molecules become available for complex formation, which subsequently diminishes the solubility of the surface layer, leading to improved inhibiting effect [15].

The increase in efficiency of inhibition with concentration indicates that more lysine molecules are adsorbed on the metal surface at higher concentration, leading to greater surface coverage. The reduced effectiveness is observed at low inhibitor concentrations, including the relatively small molecular area of lysine. It is generally accepted that the first step in the adsorption of an organic inhibitor on a metal surface usually involves the replacement of one or more water molecules adsorbed at the metal surface [18].

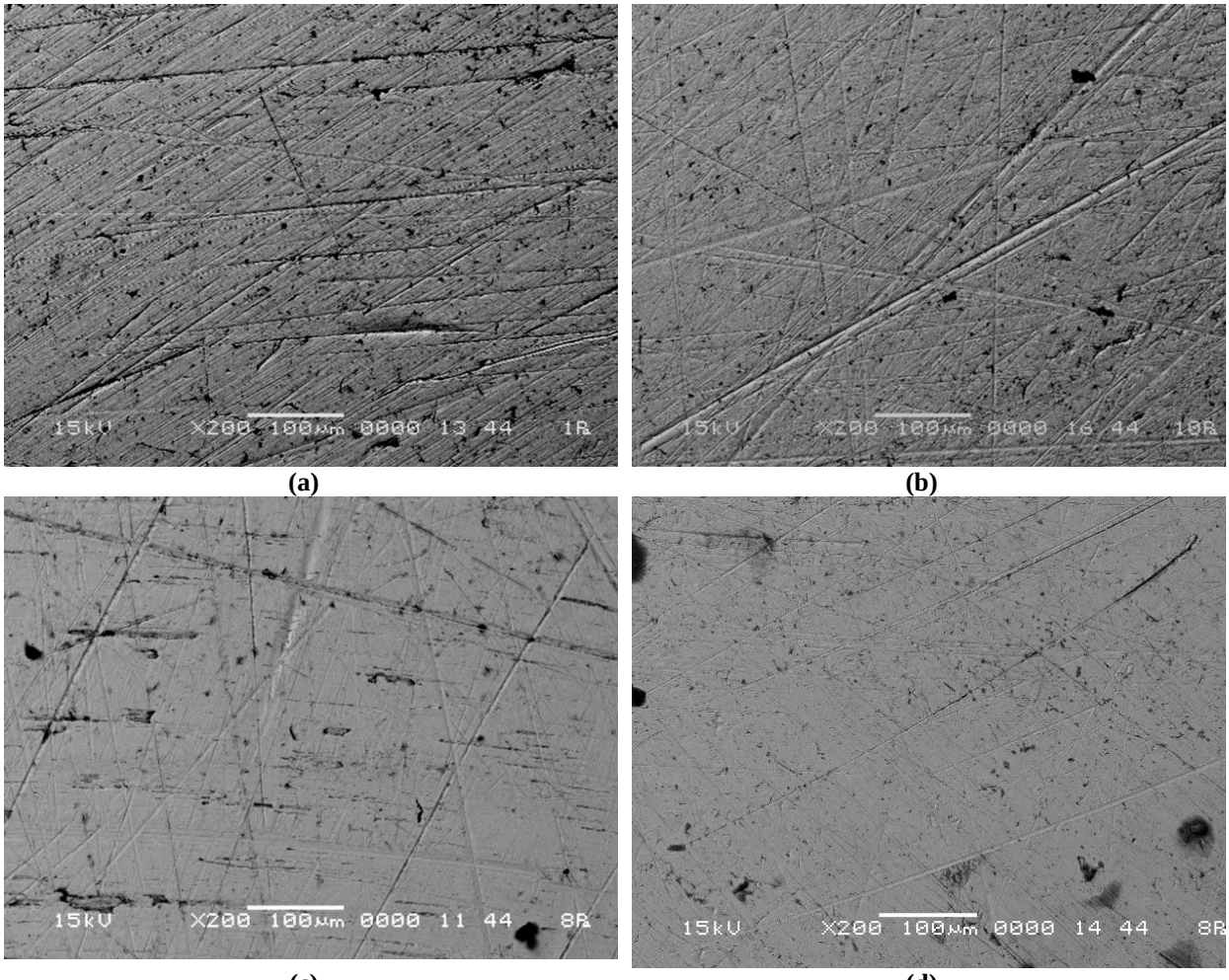
$$Inh_{(sol.)} + x\ H_2O_{(ads.)} \rightleftharpoons Inh_{(ads.)} + x\ H_2O_{(sol.)}$$

The inhibitor may then combine with freshly generated Fe^{2+} ions on the stainless steel surface, forming metal - inhibitor complex[18]:

$$Fe \longrightarrow Fe^{2+} + 2e^{-}$$

$$Fe^{2+} + Inh_{(ads.)} \longrightarrow [Fe\text{-}Inh]^{2+}_{(ads.)}$$

The adsorption behaviour of various amino acids on 316L stainless steel surface was investigated [19]. These investigations suggest that the acidic and basic amino acids are adsorbed through two electrostatic interactions of two ionized groups in the amino acid with 316L stainless steel surface. However, it has been reported that the number of –OH groups on the stainless steel surface is nearly the same regardless of the crystal forms of the metal oxide on the surface and thickness of the passive films [20,21]. The calculated configurations for the basic amino acids such as lysine and arginine show that the symmetric axis of $–NH_3^+$ groups and the guanidine groups of the basic amino acids are directed to O^-. Such orientations of the anionic and cationic groups of the acidic and basic amino acids were quite consistent with those indicated by the results from FT-IR analyses [19].



(a) **(b)** **(c)** **(d)**

Fig. 4. SEM images of 316L stainless steel surface at 200 magnification, (a) polished surface, (b) stainless steel surface after immersion 2 hr in 0.5 M H_2SO_4 solution without lysine, (c) stainless steel surface after immersion 2 hr in 0.5 M H_2SO_4 containing 5 x10^{-3} M lysine,(d) stainless steel surface after immersion 2 hr in 0.5 M H_2SO_4 containing 7 x 10^{-2} M lysine.

3-4- SEM analysis

The surface morphology of 316L stainless steel studied by scanning electron microscopy (SEM), surface was observed after 2 hs of immersion in 0.5 M H_2SO_4 at room temperature before and after addition of inhibitor corrosion (lysine). Fig. 4a shows the polished surface of 316L stainless steel before being exposed to the testing environment, it was observed as a uniform surface along with the presence of dark spots. Fig. 4b shows the SEM image after immersion in 0.5 M H_2SO_4 (Blank solution) without lysine, showing presence of small number of pits. These results is in agreement with Refaey *et al.* [22]. These results show that, the pitting corrosion of 316L stainless steel depends on the acid concentration. The increase of H_2SO_4 concentration leads to increase of pitting potential towards the more positive direction, i.e. decrease of the pitting corrosion [22]. SEM investigations of the 316L stainless steel surface, data showed that the surface was covered with a lower pit density for H_2SO_4 [22]. Fig. 4 (c and d), shows the stainless steel surface protects after adding lower and higher concentration (5×10^{-3} & 7×10^{-2}) of lysine , respectively. It is observed that, the protective film is thicker in case of higher concentration of lysine than in case of its lower concentration. These results are in agreement with the above discussion.

4- Conclusion

From the above studies, it can be concluded that:

1- Lysine is a good cathodic inhibitor for corrosion of stainless steel in 0.5 M H_2SO_4 solution.
2- Corrosion inhibition efficiency of lysine increases with increasing its concentration and reaches a maximum value at 7×10^{-2} M.
3- Corrosion inhibition by lysine takes place by adsorption of the inhibitor on the metal surface and formation of a protective layer (Fe-lysine complex film) on the metal surface.
4- The SEM images confirm the inhibitive character of lysine and the degree of inhibition increases with increase in concentration.

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