

## Inhibitive Effect of L-Lysine on the Corrosion of Mild Steel in Acidic Solutions

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The inhibition performance and mechanism of L-lysine for the corrosion of mild steel in acidic solutions were investigated using electrochemical measurements and Quantum chemical calculation. The results revealed that L-lysine acted as a mixed-type inhibitor with a predominantly cathodic action for mild steel in 1 M HCl solution, but as a modest cathodic inhibitor for mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. The adsorption of L-lysine on steel surface obeyed Langmuir adsorption isotherm, and the thermodynamic parameters were further determined based on the model. Moreover, quantum chemical calculation gave further insight into the mechanism of inhibition of L-lysine. Besides, the synergistic inhibition effect of L-lysine and chloride ion was also observed for the corrosion of mild steel.

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**Keywords:** Mild steel; L-lysine; Acidic solutions; Adsorption isotherm; Quantum chemical calculation.

### 1. INTRODUCTION

Organic inhibitors are commonly used to inhibit the corrosion of metals in aggressive media, especially in acidic solutions. However, most of organic inhibitors are synthetic chemicals, expensive and very hazardous to both human health and the environment, thus, the development of non-toxic or low-toxic inhibitors has received much attention in current research [1-5]. Thereinto, amino acids are known to be a kind of effective non-toxic inhibitor for metallic materials in corrosive media [1,6-12]. Bobina and co-workers reported the inhibitory properties of L-histidine on the corrosion of carbon steel in weak acid media containing acetic acid/sodium acetate [11]. Mendonça et al. evaluated six amino acids as corrosion inhibitors for carbon steel and copper in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution through electrochemical techniques and theory computations [9]. Some amino acids as inhibitors for copper

corrosion in 8 M phosphoric acid at different temperatures were investigated [1]. And, the synergistic inhibition effect of imidazoline derivative and L-cysteine on carbon steel corrosion in a CO<sub>2</sub>-saturated brine solution was studied by Zhao's research group [12]. Moreover, the corrosion inhibition of amino acid derivatives such as amino acid-derived ionic liquid [13], Schiff's bases [14,15] and nonionic surfactants [16] was also researched. L-lysine is a basic amino acid, containing two amino groups and a carboxyl group, which could be seemed as an effective potential inhibitor. And the results have been shown that organic inhibitors exhibit different corrosion inhibition performance in different acid solutions [17,18], but there are few reports on amino acids in this field. In present work, electrochemical techniques are employed to investigate the inhibition effect of L-lysine on the corrosion of mild steel in 1 M HCl solution and 0.5 M H<sub>2</sub>SO<sub>4</sub> solution, respectively. Moreover, the inhibition mechanism of L-lysine and the influence of chloride ion on the inhibitory effect of L-lysine are also discussed.

## 2. EXPERIMENTAL

### 2.1. Electrolyte and Material

The 0.5 M H<sub>2</sub>SO<sub>4</sub> and 1 M HCl solutions were prepared using distilled water with analytical grade sulphuric acid and hydrochloric acid, respectively. L-lysine was purchased from Shanghai Ru Ji Biological Technology Development Co. Ltd. The chemical composition (in wt%) of mild steel as follows: C (0.16%), Si (0.18%), Mn (0.29%), P (0.014%), S (0.013%) and Fe for balance. The steel sample was cut into 10 mm × 5 mm with an exposed surface area of 0.785 cm<sup>2</sup>, while the remainder was embedded by epoxy. Prior to experiments, the sample was grinded by SiC abrasive paper (200,400, 600 and 800 grade), then rinsed with distilled water, degreased in acetone and dried at room temperature.

### 2.2. Electrochemical Measurements

Electrochemical experiments were conducted through the conventional three-electrode system using CHI660E electrochemical workstation (Shanghai Chenhua Instrument Co. Ltd.), in which the auxiliary electrode and reference electrode was the platinum electrode and saturated calomel electrode (SCE), respectively. In the experiments, the solution temperature was controlled by a constant temperature water bath with an accuracy of 1 K, and the electrolytic cell was open to the air and under a static condition.

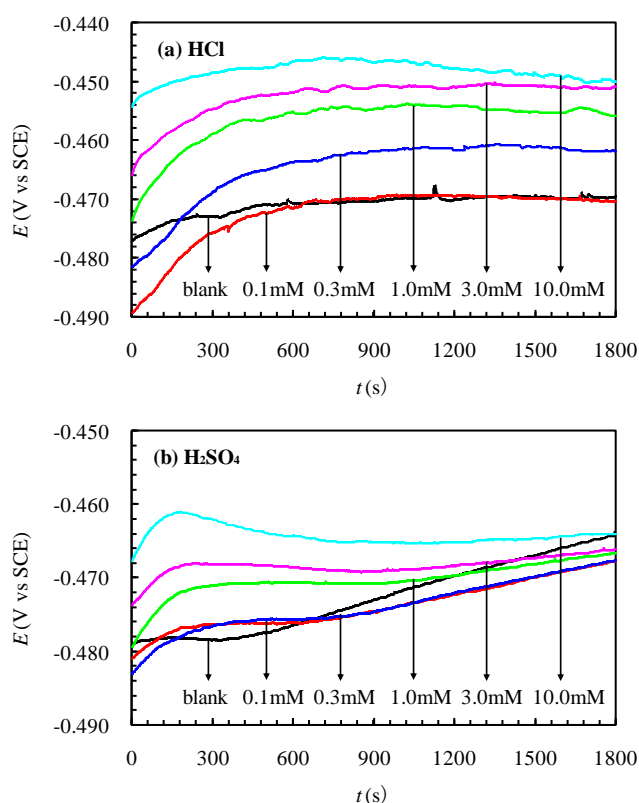
Before measuring electrochemical impedance spectroscopy (EIS), the open circuit potential (OCP) of steel electrode in test solution was monitored for 30 minutes, then the electrochemical impedance spectroscopy was measured using AC signals 5 mV peak to peak in the frequency range from 10<sup>-2</sup> Hz to 10<sup>5</sup> Hz. At last, the polarization curve was obtained by potentiodynamic scanning method in the potential range from -250 to +250 mV relative to OCP with a scan rate of 0.5 mV/s.

### 2.3. Quantum Chemical Calculations

Quantum chemical calculation was conducted through Gaussian G09 program using the B3LYP method of density functional theory (DFT) at the basis set level of 6-311++G(d,p). The molecular structure of L-lysine was geometrically optimized, and related quantum chemical parameters, including the energy of the highest occupied molecular orbital ( $E_{\text{HOMO}}$ ), the energy of the lowest unoccupied molecular orbital ( $E_{\text{LUMO}}$ ), energy gap ( $\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$ ), fraction of electrons transferred ( $\Delta N$ ) and dipole moment ( $\mu$ ), were calculated.

## 3. RESULTS AND DISCUSSION

### 3.1. OCP-Time Curves



**Figure 1.** OCP-time curves of mild steel in 1 M HCl (a) and 0.5 M H<sub>2</sub>SO<sub>4</sub> (b) solutions without and with different concentrations of L-lysine at 298 K.

The variation of the open circuit potential of steel electrode with time in the test solution is presented in Figure 1. Figure 1(a) shows the OCP of mild steel in HCl solution increases gradually and finally approaches to a steady state, and the OCP value increases with the increase in the concentration of L-lysine, which indicate that L-lysine may influence the anodic reaction of mild steel in HCl solution [19-20]. However, the OCP of mild steel in H<sub>2</sub>SO<sub>4</sub> solution, as shown in Figure 1(b), is continuously increasing until the concentration of corrosion inhibitor higher than 3.0 mM, but the addition of L-lysine reduces the growth rate of potential. A more negative OCP observed in the

absence of L-lysine indicates that L-lysine has influenced the cathodic reaction of mild steel in H<sub>2</sub>SO<sub>4</sub> solution [19-20]. Obviously, the different change trends of OCP reflect the differences in corrosion mechanism of mild steel in two kinds of acid solutions.

### 3.2. Potentiodynamic Polarization Curves

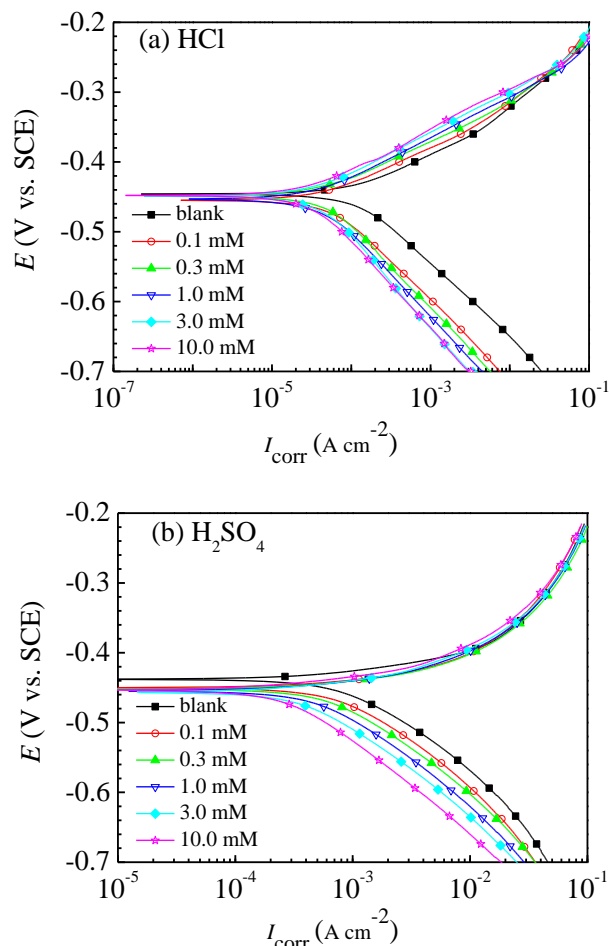
Figure 2(a) shows the potentiodynamic polarization curves for mild steel in 1 M HCl solution without and with different concentrations of L-lysine at 298 K, from which it can be clearly seen that adding L-lysine leads to the anodic branch and cathodic branch of the polarization curves shift to the direction of low current density, and the current density decreases with increasing inhibitor concentration, which indicate that L-lysine inhibits both the anodic dissolution of mild steel and the cathodic reduction of hydrogen ions, but obviously the inhibitory effect of L-lysine on the cathode reaction is greater than that on the anode reaction. Moreover, there is obvious Tafel region in the polarization curves. Thus, the related electrochemical parameters such as corrosion potential ( $E_{\text{corr}}$ ), corrosion current density ( $I_{\text{corr}}$ ), and Tafel slopes of anode ( $\beta_a$ ) and cathode ( $\beta_c$ ) are determined by Tafel extrapolation [21-23], and are listed in Table 1. Subsequently, the inhibition efficiency ( $\eta$ ) is calculated by the following equation [22-23]:

$$\eta(\%) = \left(1 - \frac{I_{\text{corr}}}{I_{\text{corr},0}}\right) \times 100 \quad (1)$$

where,  $I_{\text{corr},0}$  and  $I_{\text{corr}}$  is the corrosion current density of mild steel electrode in the uninhibited and inhibited solutions, respectively.

However, the polarization curves of mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution, as shown in Figure 2(b), display that the cathodic reaction of the corrosion of mild steel is inhibited when L-lysine is added to the H<sub>2</sub>SO<sub>4</sub> solution, and the inhibition increases with the increase of inhibitor concentration, but the anodic polarization curves almost overlap together and do not exist the Tafel linear region, therefore, the electrochemical parameters are determined by Tafel extrapolation of the cathodic polarization curves to the  $E_{\text{corr}}$  [24], and are listed in Table 1.

Table 1 illustrates that the value of  $I_{\text{corr}}$  decreases, accordingly, the inhibition efficiency ( $\eta$ ) is improved, when the L-lysine concentration is increased, and the inhibitive effect of L-lysine on the corrosion of mild steel in HCl solution is better than that in H<sub>2</sub>SO<sub>4</sub> solution. Meanwhile, the values of  $E_{\text{corr}}$  do not change significantly, although the  $E_{\text{corr}}$  of steel electrode in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution becomes more negative with the incremental inhibitor concentration, but the displacement is less than 20 mV. Moreover, considering the values of  $\beta_a$  and  $\beta_c$  are slightly changed, it can be thought that the presence of L-lysine has little influence on the corrosion mechanism of mild steel in the test solutions, namely, the inhibition of L-lysine is based on the geometric blocking effect [18,25]. As suggested above, L-lysine can be seen as a mixed-type inhibitor with a predominantly cathodic action for mild steel in HCl solution [26], but a modest cathodic inhibitor for mild steel in H<sub>2</sub>SO<sub>4</sub> solution [27].



**Figure 2.** Potentiodynamic polarization curves of mild steel in 1 M HCl (a) and 0.5 M H<sub>2</sub>SO<sub>4</sub> (b) solutions without and with different concentrations of L-lysine at 298 K.

**Table 1.** The electrochemical parameters for mild steel in 1 M HCl and 0.5 M H<sub>2</sub>SO<sub>4</sub> solution without and with different concentrations of L-lysine at 298 K.

System	C(mM)	$E_{corr}$ (V vs. SCE)	$I_{corr}$ (mA cm <sup>-2</sup> )	$\beta_a$ (mV dec <sup>-1</sup> )	$-\beta_c$ (mV dec <sup>-1</sup> )	$\eta$ (%)
1 M HCl	blank	-0.446	0.117	55.0	103.4	\
	0.1	-0.448	0.065	53.5	101.3	43.8
	0.3	-0.448	0.047	54.1	123.4	60.0
	1.0	-0.453	0.040	59.4	120.1	65.8
	3.0	-0.449	0.039	59.3	135.9	66.3
	10.0	-0.448	0.035	66.1	124.4	70.2
0.5M H <sub>2</sub> SO <sub>4</sub>	blank	-0.438	0.853	\	119.4	\
	0.0001	-0.450	0.766	\	123.8	10.3
	0.0003	-0.452	0.608	\	119.5	28.7
	0.001	-0.455	0.491	\	120.4	42.5
	0.003	-0.456	0.356	\	116.4	58.2
	0.01	-0.458	0.312	\	121.9	63.4

### 3.3. Electrochemical Impedance Spectroscopy (EIS)

Figures 3 and 4 show the Nyquist (a) and Bode (b) plots of mild steel obtained in 1 M HCl and 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions without and with different concentrations of L-lysine at 298 K, respectively. It can be seen from Figures 3(a) and 4(a) that the addition of L-lysine has little influence on the shapes of Nyquist plots, except that the diameter of capacitive loop significantly enhances with the increase in L-lysine concentration, which suggest the presence of L-lysine dose not change the corrosion mechanism of mild steel in test solutions [28-29], and that is consistent with the analytical results of polarization curves. Nyquist plots in Figure 3(a) show a depressed capacitive loop due to the roughness and inhomogeneity of electrode surface [2,30], but in Figure 4(a) is composed of a capacitive loop at high frequencies (HF) and an inductive loop at low frequencies (LF), which may reflect the difference of corrosion mechanism of mild steel in HCl and H<sub>2</sub>SO<sub>4</sub> solutions. The capacitive loop is usually considered to correspond to the time constant of charge transfer and double layer capacitance ( $C_{dl}$ ) [31], while the LF inductive loop may be attributed to the relaxation process caused by adsorption species such as  $(SO_4^{2-})_{ads}$  and  $(H^+)_{ads}$  on the electrode surface [2,32-33]. Figures 3(b) and 4(b) show the values of phase angle and impedance magnitude ( $|Z|$ ) increase with the increasing of L-lysine concentration, which indicate better protection of inhibitor with higher concentrations [22].

Based on the above mentioned discussion and description, the impedance parameters are obtained by fitting the EIS to the equivalent circuits as shown in Figure 5 using ZSimpWin software, and are given in Table 2. In the circuits,  $R_s$  is the resistance of solution,  $L$  and  $R_L$  represent the inductive element and inductive resistance, respectively.  $R_{ct}$  is the charge transfer resistance, and due to the imperfections of the surface, constant phase element (CPE) is usually used to replace double layer capacitance ( $C_{dl}$ ) [34-35], and CPE can be described as follows [34,36]:

$$Z_{CPE} = \frac{1}{Y_0(j\omega)^n} \quad (2)$$

where  $Y_0$  is the CPE constant,  $j$  is the imaginary unit,  $\omega$  is the angular frequency, and  $n$  is the deviation parameter, which is often related to the surface morphology. The  $C_{dl}$  value and inhibition efficiency ( $\eta$ ) is respectively calculated according to the following equations [30,33]:

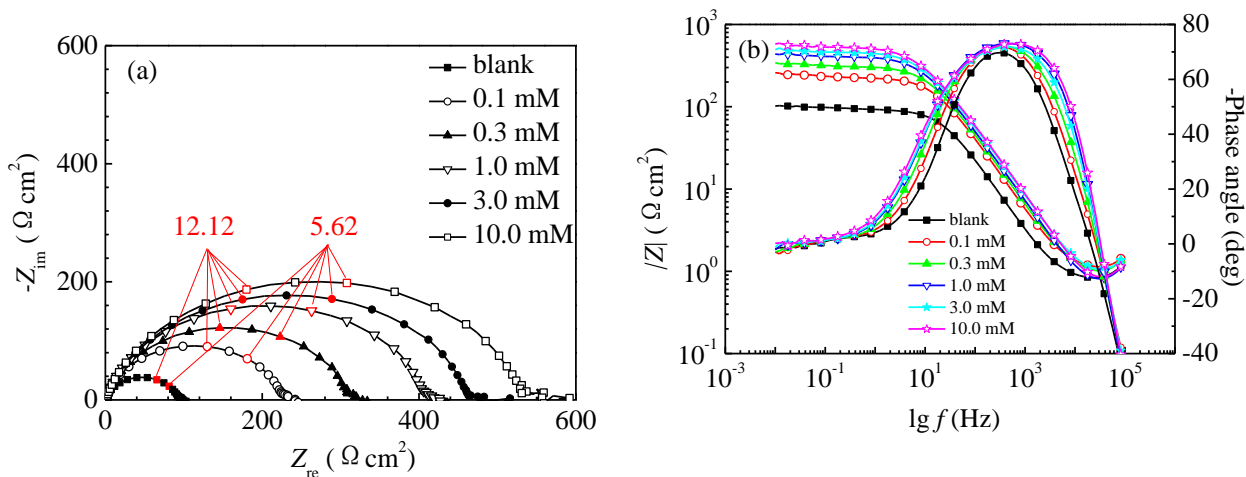
$$C_{dl} = Y_0(\omega_{max})^{n-1} = Y_0(2\pi f_{Z_{im-max}})^{n-1} \quad (3)$$

$$\eta = \frac{R_{ct} - R_{ct,0}}{R_{ct}} \times 100 \quad (4)$$

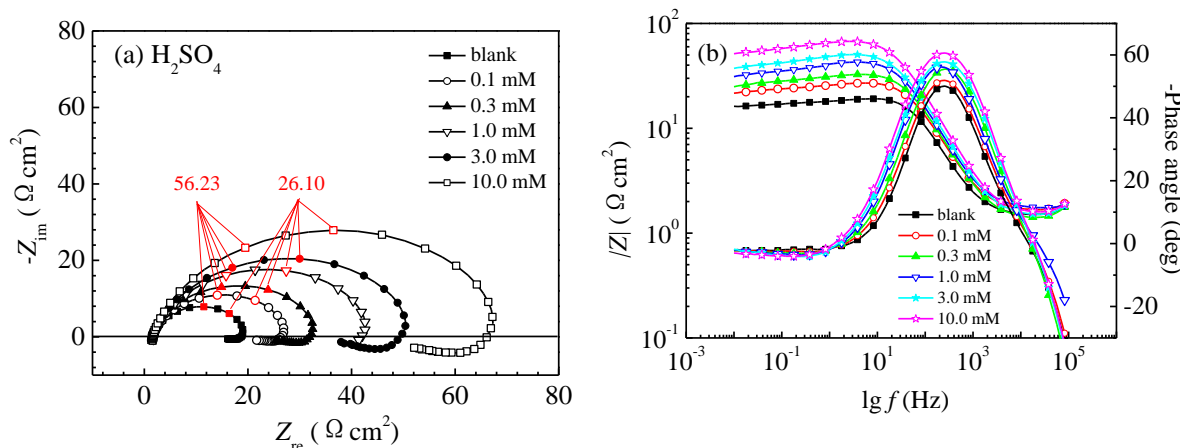
where,  $R_{ct,0}$  and  $R_{ct}$  is the charge transfer resistance without and with inhibitor, respectively.

Table 2 shows that the  $R_{ct}$  values increase, and the values of  $C_{dl}$  decrease with increasing L-lysine concentration, correspondingly, the inhibition efficiencies go up, which are attributed to the increase of surface coverage caused by the L-lysine adsorption on the mild steel surface [37-38]. The value of  $n$  is close to one, indicating the charge transfer process controls the dissolution mechanism of mild steel in test solution [37-38]. And, the inhibition efficiencies are in good agreement with those obtained from polarization curves. In addition, the inhibition efficiency of L-lysine is compared with that of other amino acids reported in literature [9,39], the related data are listed in Table 3. It can be seen that the inhibition efficiency of L-lysine is slightly less than that of two sulfur amino acids (L-cysteine and L-methionine ) in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution, but higher than that of containing amide group

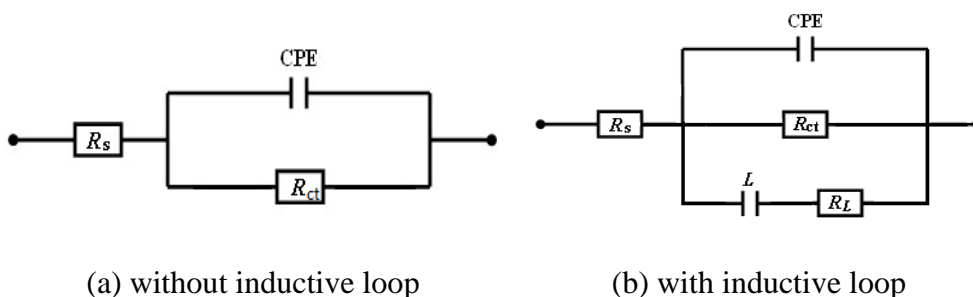
amino acids (L-glutamine and L-asparagine) and another basic amino acid L-arginine. However, in 1 M HCl solution, L-lysine exhibits good inhibition property, its inhibition efficiency is higher than that of L-cysteine and hydroxyl containing L-serine, but still below that of L-tryptophan and L-histidine, which may be attributed to the nitrogen heterocyclic ring in their molecules.



**Figure 3.** Nyquist plots (a) and Bode plots (b) for mild steel in 1 M HCl solution without and with different concentrations of L-lysine at 298 K.



**Figure 4.** Nyquist plots (a) and Bode plots (b) for mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution without and with different concentrations of L-lysine at 298 K.



**Figure 5.** Equivalent circuits used to fit the EIS without (a) and with (b) inductive loop.

**Table 2.** The EIS parameters for mild steel in test acid solutions without and with different concentrations of L-lysine at 298 K.

System	C (mM)	R <sub>s</sub> (Ω cm <sup>2</sup> )	Y <sub>0</sub> ×10 <sup>-6</sup> (S s <sup>n</sup> cm <sup>-2</sup> )	n	R <sub>ct</sub> (Ω cm <sup>2</sup> )	C <sub>dl</sub> (μF cm <sup>-2</sup> )	L (Ω cm <sup>2</sup> )	R <sub>L</sub> (Ω cm <sup>2</sup> )	η (%)
1 M HCl	blank	0.5	155.9	0.87	96	82.0	\	\	\
	0.1	1.3	69.8	0.91	229	45.8	\	\	58.1
	0.3	1.2	67.0	0.90	311	42.7	\	\	69.1
	1.0	1.0	61.6	0.89	406	40.6	\	\	76.4
	3.0	1.2	60.5	0.88	459	37.8	\	\	79.1
	10.0	1.0	57.3	0.88	527	36.9	\	\	81.8
0.5 M H <sub>2</sub> SO <sub>4</sub>	blank	1.6	217.6	0.92	17.7	133.1	26	109	\
	0.1	1.8	205.6	0.89	25.5	113.0	50	129	30.6
	0.3	1.6	182.0	0.90	31.0	105.9	79	142	42.9
	1.0	1.8	203.7	0.88	42.0	103.7	60	140	57.9
	3.0	1.6	182.4	0.88	49.3	95.6	107	178	64.1
	10.0	1.7	147.7	0.89	66.2	82.4	204	257	73.3

**Table 3.** The inhibition efficiencies obtained from EIS at amino acid concentration of 10.0 mM.

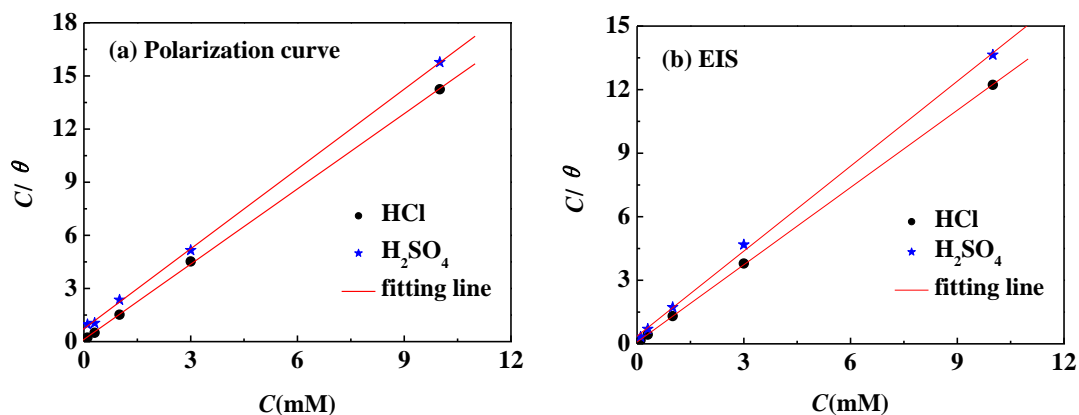
Medium	Amino acid	η(%)	Material	Temperature	Reference
1 M HCl	L-lysine	81.8	mild steel, described in Section 2.1	25 °C	\
	L-cysteine	80.5	mild steel with composition (wt%) of C(0.18), Mn(0.64), P(0.05), S(0.06) and Fe balance	25 °C	[39]
	L-serine	47.6			
	L-tryptophan	94.1			
	L-histidine	90.3			
0.5 M H <sub>2</sub> SO <sub>4</sub>	L-lysine	73.3	mild steel, described in Section 2.1	25 °C	\
	L-cysteine	81.5	carbon steel, the component not stated	at room temperature (≈ 25 °C)	[9]
	L-serine	72.6			
	L-methionine	85.9			
	L-asparagine	61.2			
	L-glutamine	53.1			
	L-arginine	43.2			

### 3.4. Adsorption Isotherm

It is well known that the corrosion inhibition effect of organic molecules is determined by their adsorption on the metal surface [40], while the adsorption isotherm can provide important information on the interaction between the inhibitor and the metal surface. In this study, the adsorption of L-lysine is found to obey the Langmuir adsorption isotherm. Langmuir isotherm can be described by equation 5 [41], in which, C is the concentration of L-lysine, K<sub>ads</sub> is the adsorption equilibrium constant, θ is the surface coverage, its value is determined by the ratio η /100.

$$\frac{C}{\theta} = C + \frac{1}{K_{ads}} \tag{5}$$





**Figure 6.** Langmuir isotherm plots for mild steel in acid solutions with different concentrations of L-lysine at 298 K.

Figure 6 shows the plots of  $C/\theta$  as function of  $C$  yield a straight line, and the correlation coefficients ( $R^2$ ) are greater than 0.998. Then, the value of  $K_a$  is obtained from the intercept of the fitting straight line, and the corresponding standard free energy of adsorption process is calculated by the following equation:

$$K_{ads} = \frac{1}{55.5} \exp\left(-\frac{\Delta G_{ads}^\ominus}{RT}\right) \tag{6}$$

where,  $R$  is the universal gas constant  $T$  is the thermodynamic temperature, and the value of 55.5 is the molar concentration of water in test solution.

Table 4 shows the values of  $K_{ads}$  are relatively large, and the values of  $\Delta G_{ads}^\ominus$  are negative, which indicate there is a strong interaction between L-lysine and the steel surface, and the adsorption process is spontaneous. Moreover, it is also noted the  $K_{ads}$  value as well as the absolute value of  $\Delta G_{ads}^\ominus$  in HCl solution is greater than that in  $H_2SO_4$  solution, which reflect the adsorption affinity of L-lysine onto the mild steel surface in HCl solution is stronger, and thus L-lysine exhibits a better inhibitive performance in HCl solution.

**Table 4.** The adsorption parameters for mild steel in acid solutions with different concentrations of L-lysine at 298K.

System	Polarization curve		EIS	
	$K_{ads}(L/mol)$	$\Delta G_{ads}^\ominus$ (kJ/mol)	$K_{ads}(L/mol)$	$\Delta G_{ads}^\ominus$ (kJ/mol)
1 M HCl	$7.99 \times 10^3$	-32.21	$1.18 \times 10^4$	-33.17
0.5 M $H_2SO_4$	$1.36 \times 10^3$	-27.84	$2.74 \times 10^3$	-29.56

### 3.5. Theoretical Calculation

The optimized geometric structure and the distributions of electrostatic potential, HOMO and LUMO of L-lysine obtained from quantum chemistry calculation through Gaussian 09 software are shown in Figure 7, and the calculated quantum chemical parameters are given in Table 5. As shown in

Figures 7(c) and 7(d), the electron density distributions of frontier molecular orbital of L-lysine are located on the amino group (-NH<sub>2</sub>) and the carboxyl group (-COOH), suggesting that N atom and O atom are the active adsorption sites of L-lysine molecule, this also can be confirmed by the distribution of electrostatic potential shown in Figure 7(b). Based on the  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$ , the value of  $\Delta N$  calculated by equation 7-9 [42] is greater than zero, which indicates that L-lysine molecule can donate electrons to mild steel surface promoting the formation of adsorptive bonds. While, the HOMO of molecule is often associated with the electron donating ability, and considering the distribution of HOMO in Figure 7(c), therefore, L-lysine is more likely to adsorb on the surface of mild steel by the amino group, especially the amino group at the end of L-lysine. Moreover, the value of  $\mu$  of L-lysine molecule is higher than that of H<sub>2</sub>O [43], due to the dipole-dipole interaction between molecules and metal surface, the L-lysine molecules can replace the water molecules adsorbed on the mild steel surface, and then play a role in inhibition the corrosion of mild steel.

$$\chi = \frac{I + A}{2} \quad (7)$$

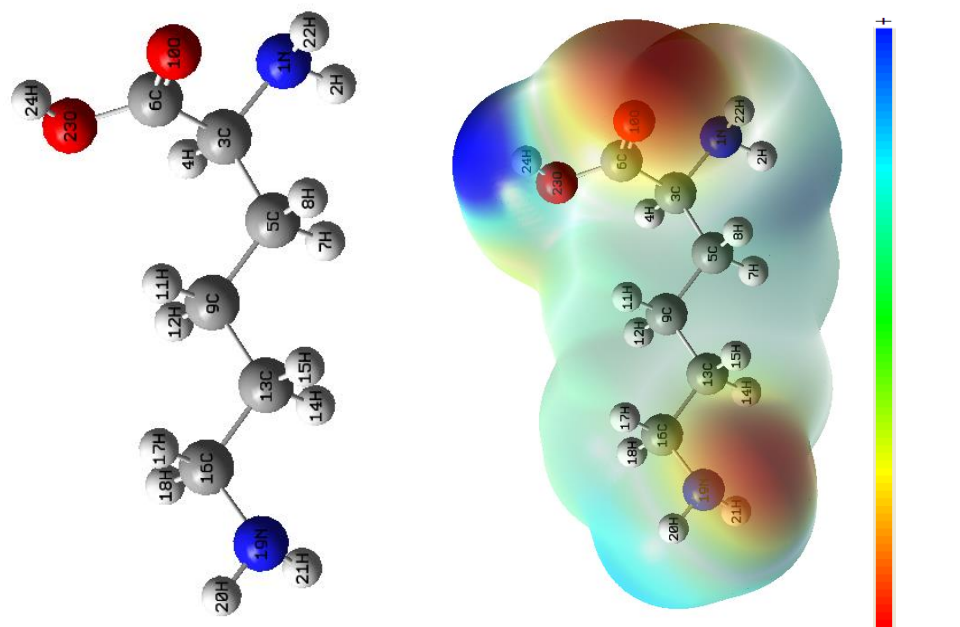
$$\gamma = \frac{I - A}{2} \quad (8)$$

$$\Delta N = \frac{\chi_{\text{Fe}} - \chi_{\text{inhibitor}}}{2(\gamma_{\text{Fe}} + \gamma_{\text{inhibitor}})} \quad (9)$$

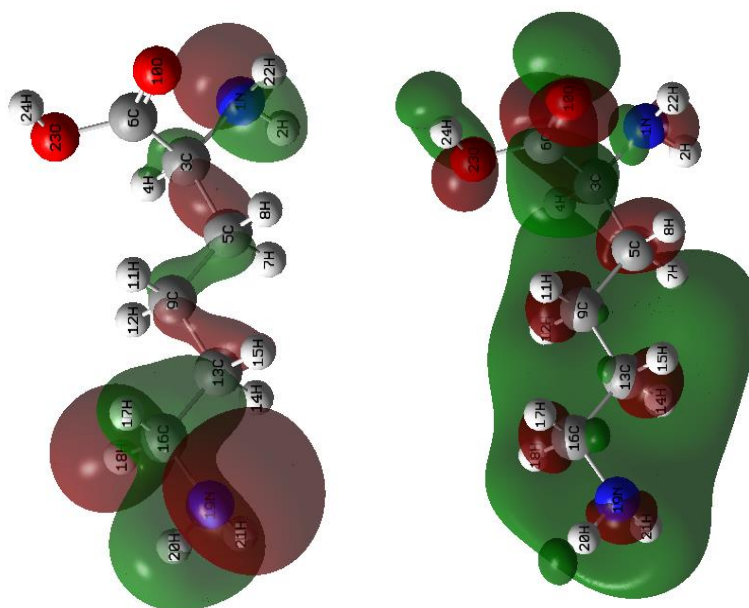
where,  $I$  is the ionization potential,  $A$  is the electron affinity, and they are defined as  $I = -E_{\text{HOMO}}$  and  $A = -E_{\text{LUMO}}$ .  $\chi$  is the absolute electronegativity, and  $\gamma$  is the global hardness. According to the literature [42,44], the theoretical values of  $\chi_{\text{Fe}}$  and  $\gamma_{\text{Fe}}$  are 7 eV and 0 eV, respectively.

### 3.6. Inhibition Mechanism of L-lysine and Its Synergistic Effect with Chlorine Ion

Generally, the inhibition mechanism of organic molecules on the corrosion of metal in acid solution is based on the adsorption of molecules on the metal surface. In acid medium, the protonated L-lysine molecules can directly adsorb on the cathodic sites of the surface of mild steel and decrease the reaction rate of cathodic hydrogen reduction. However, the protonation makes the adsorption of L-lysine on the anodic sites of the mild steel surface become difficult, and previous studies have demonstrated that the steel surface charges positive charge in acid solution [45-46]. But, the surface charge could be changed by the specific adsorption of the anion such as chloride ion (Cl<sup>-</sup>), then resulting in the joint adsorption of the anion with the protonated inhibitor molecule [47], while the specific adsorption of sulfate ions (SO<sub>4</sub><sup>2-</sup>) on the steel surface rarely occur. Thus, the cathodic reaction as well as the anodic reaction of mild steel in HCl solution is inhibited by L-lysine, but L-lysine only inhibits the cathodic reaction of mild steel in H<sub>2</sub>SO<sub>4</sub> solution. As a result, the inhibition performance of L-lysine on the corrosion of mild steel in HCl solution is better than that in H<sub>2</sub>SO<sub>4</sub> solution.



(a) optimized geometric structure (b) distribution of electrostatic potential

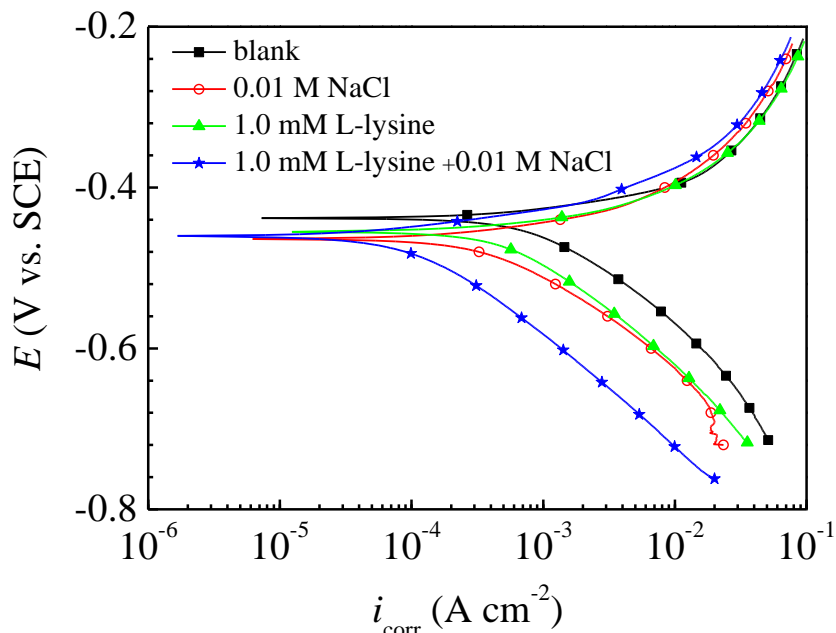


(c) distribution of HOMO (d) distribution of LUMO

**Figure 7.** The optimized geometric structure (a) and the distribution of electrostatic potential HOMO (b) and LUMO (c) of L-lysine.

**Table 5.** The quantum chemistry parameters of L-lysine.

$E_{HOMO}(eV)$	$E_{LUMO}(eV)$	$\Delta E(eV)$	$\mu(D)$	$\Delta N$
-6.70	-0.44	6.26	2.93	0.55



**Figure 8.** Polarization curves for mild steel in different test solutions at 298 K.

**Table 5.** The electrochemical parameters for mild steel in different test solutions at 298 K.

System	$E_{\text{corr}}$ (V vs. SCE)	$I_{\text{corr}}$ (mA cm <sup>-2</sup> )	$-\beta_c$ (mV dec <sup>-1</sup> )	$\eta$ (%)	$S$
blank	-0.438	0.853	119.4	\	\
0.01 M NaCl	-0.464	0.389	107.4	54.4	\
1.0 mM L-lysine	-0.455	0.491	120.4	42.5	\
1.0 mM L-lysine+0.01 M NaCl	-0.460	0.096	120.0	88.7	2.32

Furthermore, in order to confirm the specific adsorption of Cl<sup>-</sup>, the effect of chloride ions on the corrosion of mild steel in H<sub>2</sub>SO<sub>4</sub> solution and its effect on the corrosion inhibition of L-lysine are determined by potentiodynamic polarization technique, the results show in Figure 8, and the corrosion parameters obtained by Tafel extrapolation method are listed in Table 5. Figure 8 and Table 5 show the addition of sodium chloride (NaCl) mainly inhibits the cathodic reaction of mild steel in H<sub>2</sub>SO<sub>4</sub> solution, and has little influence on the anodic reaction. However, when NaCl is added in the H<sub>2</sub>SO<sub>4</sub> solution containing L-lysine, although the cathodic reaction is significantly suppressed, the anodic polarization curve is shifted to the direction of low current density, which means that the anodic reaction is inhibited due to the specific adsorption of Cl<sup>-</sup>, and the calculated synergies coefficient ( $S$ ) [33] also indicates that the synergistic inhibitive effect occurs between L-lysine and Cl<sup>-</sup> on the corrosion of mild steel in H<sub>2</sub>SO<sub>4</sub> solution. Moreover, the nearly parallel anodic polarization curve in Figure 8 illustrates that the addition of NaCl with a concentration of 0.01 M is not enough to change the anodic reaction mechanism of mild steel in the H<sub>2</sub>SO<sub>4</sub> solution containing 1.0 mM L-lysine, which is agreement with the research result of Lorenz [48].

#### 4. CONCLUSIONS

Due to the different adsorption capacity of chloride ion and sulfate ion, L-lysine acts as a mixed-type inhibitor with a predominantly cathodic action for mild steel in 1 M HCl solution, but a modest cathodic inhibitor for mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution, and there is synergistic inhibitive effect between L-lysine and Cl<sup>-</sup> on the corrosion of mild steel in H<sub>2</sub>SO<sub>4</sub> solution. Electrochemical impedance spectroscopy data reveals that the inhibitor molecules adsorb onto the mild steel surface, and the adsorption of L-lysine on the mild steel surface is spontaneous process and obeys the Langmuir adsorption isotherm. Theoretical calculations display the hetero atoms N and O, especially the N atom, are the active adsorption sites of L-lysine.

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