

Environmentally safe corrosion inhibition of Pb in aqueous solutions

N.H. Helal^b, M.M. El-Rabiee^b, Gh.M. Abd El-Hafez^b, W.A. Badawy^{a,*}

^a Chemistry Department, Faculty of Science, Cairo University, Giza, Egypt

^b Chemistry Department, Faculty of Science, Fayoum University, Fayoum, Egypt

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Abstract

The corrosion and corrosion inhibition of lead in aqueous solutions with different pHs (2, 7 and 12) were investigated. The corrosion rate was calculated in the absence and presence of the corrosion inhibitor using polarization and impedance techniques. Amino acids have been used as environmentally safe corrosion inhibitors. The inhibition efficiency of the different amino acids at a concentration of 0.025 M was calculated. Corrosion inhibition efficiency up to 87% was recorded with glutamic acid in neutral solutions. The experimental impedance data were fitted to theoretical values according to an equivalent circuit model to explain the behavior of the metal under different conditions. The corrosion inhibition process was found to depend on the adsorption of the amino acid molecules on the metal surface; and the adsorption free energy in each case was calculated. The free energy of adsorption of glutamic acid on Pb was found to be equal to -2.9 kJ/mol, which reveals that the inhibitor is physically adsorbed on the metal surface. The results are obeying Langmuir adsorption isotherm.

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1. Introduction

Lead is frequently used in chemical plants and laboratories for fume ducts, hoods, bench tops and floors [1]. Lead is also used in buildings for roofing, gutters and downspout [2]. The most important application of lead is its widespread usage in acid storage batteries [3]. For these reasons, the corrosion inhibition of lead by different organic compounds has been studied in considerable details [4–8]. Pyrazol derivatives were found to inhibit the lead corrosion in acidic chloride solutions, and the inhibition of the corrosion process was explained to be due to the stabilization of $PbCl_2$ which is formed as a barrier layer on the metal surface protecting it from continuous corrosion [9,10].

Generally, very little work has been performed on the use of amines as inhibitors for the corrosion of lead in aggressive acidic media [11]. Amino acids were reported as good corrosion inhibitors for many metals in various aggressive media [12–16]. They were tested as corrosion inhibitors for lead in

0.24 M $HClO_4$ using potentiodynamic measurements [17]. The results have shown that methionine (MET) is the best inhibitor and its corrosion inhibition efficiency reached a value of 95% at 10^{-3} M (MET). The inhibitor was found to be adsorbed on the lead surface according to Temkin isotherm model, and the corrosion inhibition efficiency ($\eta\%$) was found to be independent of temperature in the range of 30–60 °C.

The objective of the present work is to study the effect of different amino acids on the corrosion of lead in aqueous solutions of different pH (2.7 and 12). In this respect, different amino acids have been used. It is aimed at the specification of the best inhibitor and the optimum conditions for the corrosion inhibition process.

2. Experimental details

The working electrodes were made from spectroscopically pure lead 99.99% (Aldrich-Chemie). The electrode consists of massive rods, mounted into glass tubes by two-component epoxy resin leaving a surface area of 0.385 cm² to contact the solution. The cell was a three-electrode all-glass cell with a platinum counter electrode and saturated calomel reference electrode. Before each experiment, the working electrode was polished mechanically using successive grades of emery papers up to 2000 grit, rubbed with a smooth polishing cloth,

* Corresponding author.

E-mail addresses: wbadawy@wbadawy.csc.org.eg, wbadawy@Chemsci.cu.edu.eg, wbadawy50@hotmail.com (W.A. Badawy).

then washed with triple distilled water and transferred quickly to the electrochemical cell. The measurements were carried out in aqueous solutions of pH 2, 7 and 12, the solutions were prepared from analytical grade reagents and triple distilled water. The buffer solutions were prepared according to the following compositions:

pH	Composition
2	62.5 ml (0.2 M) boric acid + 62.5 ml (0.05 M) borax + 62.5 ml (0.4 M) H ₃ PO ₄ and complete into 250 ml
7	127.8 ml (0.1 M) COOKC ₆ H ₄ COOH + 122.2 ml (0.1 M) HCl and complete to 250 ml
12	100 ml (0.2 M) KH ₂ PO ₄ + 163.7 ml (0.2 M) NaOH

The electrochemical impedance investigations and polarization measurements were performed using the voltalab 10 PGZ 100 “All-in-one” potentiostat/Galvanostat system. The potentials were measured against and referred to the saturated calomel electrode (SCE). All potentiodynamic polarization measurements were carried out using a scan rate of 10 mV/s. The amino acids used in these investigations include:

1. Aliphatic amino acids: glycine, alanine and valine;
2. Sulfur containing amino acids: cysteine;
3. Acidic amino acids: glutamic acid;
4. Basic amino acids: histidine.

The corrosion current densities were measured in each case and the corrosion inhibition efficiency, η , was calculated from the values of the corrosion current densities of the metal before and after the addition of the amino acids to the corrosive medium.

3. Results and discussion

3.1. Open-circuit potential measurements

The open-circuit potentials of Pb in the absence and presence of amino acids at constant concentration of (0.025 M) were traced over 60 min from the electrode immersion in the aqueous solutions of pH 2, 7 and 12. The results are presented in Fig. 1a–c. The steady state potential is reached within the first 20 min of the electrode immersion in the test solution. In the presence of amino acids in acidic solution, the steady state potential did not show any remarkable change (cf. Fig. 1a). In the case of neutral solutions, the steady state potential gets more negative in the presence of amino acid (cf. Fig. 1b). The presence of the amino acid, especially glutamic acid in basic solutions has shifted the steady state potential towards more positive values (cf. Fig. 1c). The direction of potential shift depends on the type of the amino acid and the metal surface. The potential shift can be attributed to the adsorption of the amino acids molecules on the active sites and/or the deposition of corrosion products on the electrode surface.

3.2. Potentiodynamic polarization measurements

3.2.1. Behavior of Pb electrode in inhibitor-free aqueous solutions

The electrochemical behavior of lead was investigated under polarization conditions, the linear polarization and Tafel extrapolation techniques were used. Unless otherwise stated the

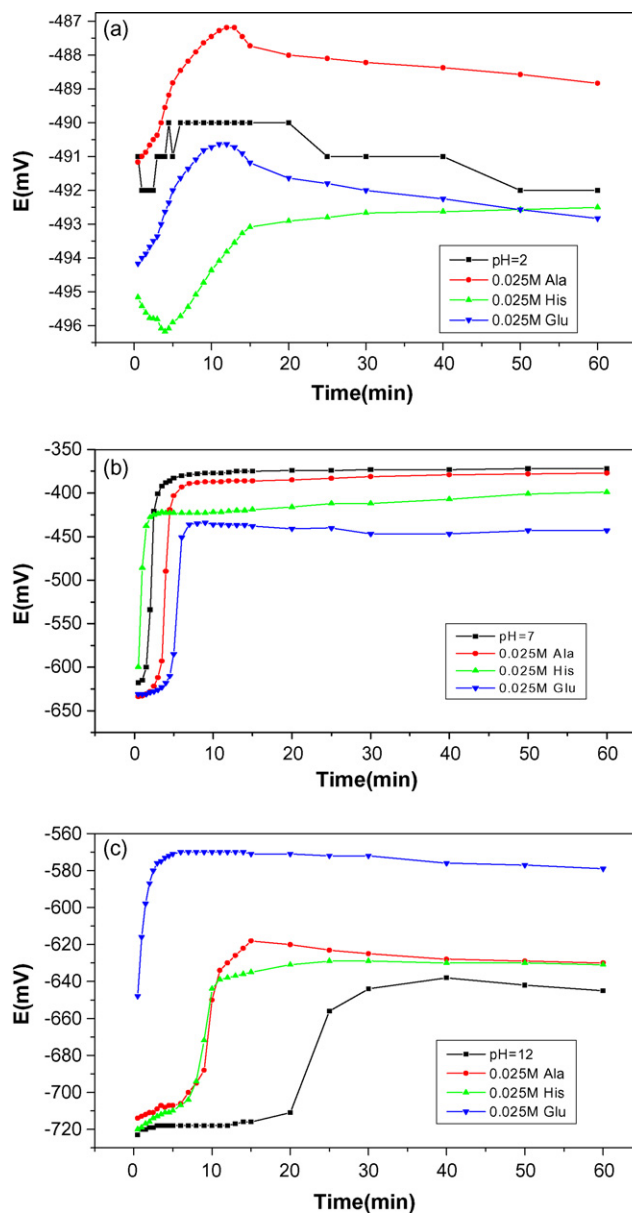


Fig. 1. Variation of the open-circuit potential with time for Pb electrode after 60 min of the electrode immersion in aqueous solutions at different pHs with different amino acids at 25 °C: (a) pH 2, (b) pH 7 and (c) pH 12.

polarization experiments were carried out at a scan rate of 10 mV/s. Fig. 2a presents the potentiodynamic polarization curves of the lead electrode after holding the metal at the open-circuit potential for 60 min in naturally aerated solutions of pH 2, 7 and 12. The effect of the solution pH on the corrosion current density is presented in Fig. 2b. It is clear that the measured current density in neutral solutions is less than the values obtained in basic and acidic solutions. In acidic solutions, the calculated value of i_{corr} reached $60.7 \mu\text{A}/\text{cm}^2$, which is more than three times that obtained in basic solutions ($15.9 \mu\text{A}/\text{cm}^2$) and about 12 times that measured in neutral solutions ($4.69 \mu\text{A}/\text{cm}^2$). The corrosion of the metal in aqueous solutions is represented by the overall two-electron transfer reaction:



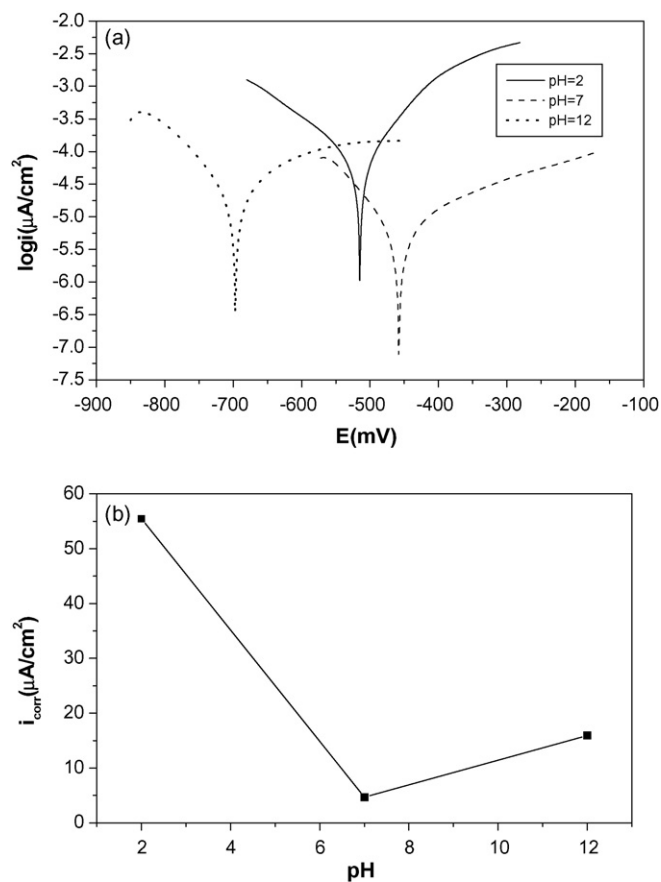
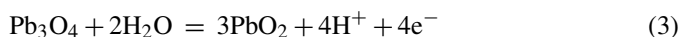


Fig. 2. (a) Potentiodynamic polarization curves of Pb after 60 min of the electrode immersion in solutions of pH 2, 7 and 12 at 25 °C. (b) Relation between corrosion current density and the pH of the electrolyte after 60 min of the electrode immersion at 25 °C.

This reaction occurs in a sequence of steps in which the formation of monovalent intermediate is possible. The formation of monovalent intermediates and corrosion products leads to the formation of a passive film, most probably of PbO. The stability of the formed oxide film on the metal surface and the rate-determining step of the corrosion/passivation process depend on the solution pH. In neutral or slightly basic solutions, the formed PbO is transformed to higher lead oxides according to:



Both Pb₃O₄ and PbO₂ are stable in neutral or basic solutions, which explains the observed passive behavior of Pb and the relatively low corrosion current values recorded in these solutions. In acidic solutions, the metal surface corrodes continuously and uniformly, since PbO cannot impart passivity in acidic solutions, it dissolves readily leading to the formation of Pb²⁺.

3.2.2. Behavior of Pb in inhibitor-containing aqueous solutions

The corrosion parameters, corrosion potential, *E*_{corr}, corrosion current density, *i*_{corr}, and the corrosion resistance, *R*_{corr}, of Pb electrode in amino acid free and amino acid containing naturally aerated stagnant aqueous solutions of different pHs (2, 7

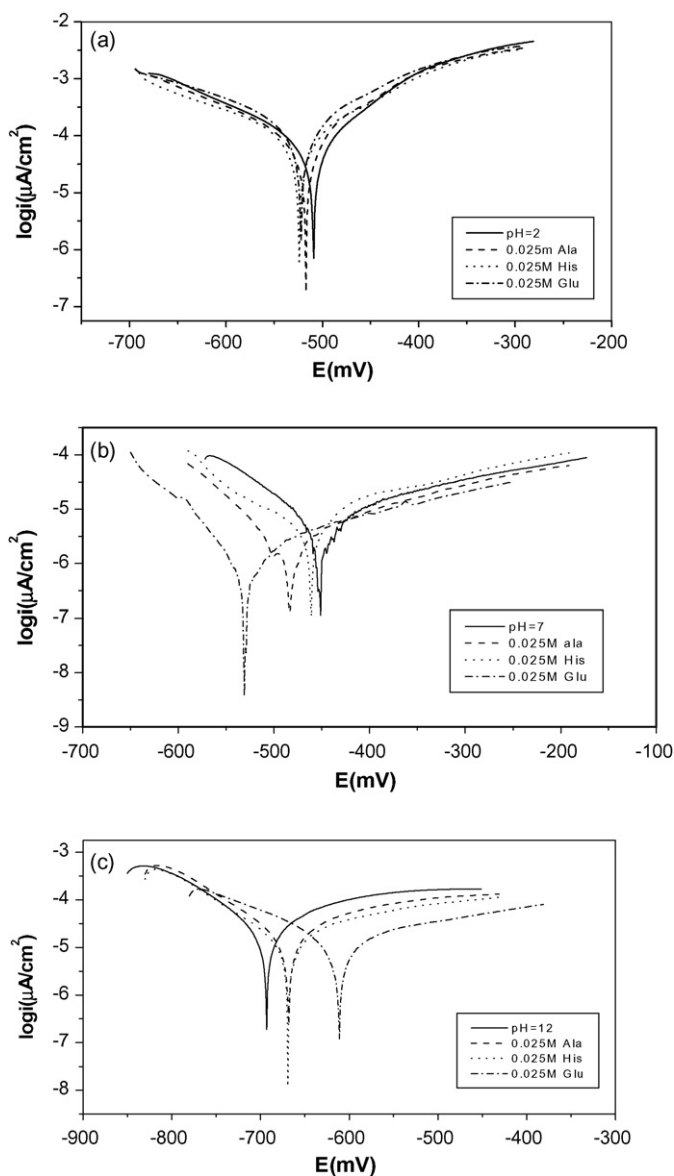


Fig. 3. Potentiodynamic polarization curves of Pb after 60 min of electrode immersion in amino acid free and amino acid containing aqueous solutions of different pH, at 25 °C: (a) pH 2, (b) pH 7 and (c) pH 12.

and 12) were calculated from the potentiodynamic polarization curves. The potentiodynamic polarization curves of Pb recorded in the amino acid free aqueous solutions of different pHs and those recorded in solutions containing a constant concentration (0.025 M) of each of three representative amino acids namely, glutamic acid, alanine and histidine are presented in Fig. 3a–c. Similar polarization curves were obtained in the presence of other amino acids like glycine, valine and cysteine (not shown). The calculated corrosion parameters of Pb in the different solutions are presented in Tables 1–3 for the acidic, neutral and basic solutions, respectively. It is clear from the potentiodynamic data that the presence of the amino acid in the solution decreases the corrosion rate, i.e. the value of *i*_{corr} decreases. The inhibition efficiency, *η*, was calculated from the values of the corrosion current density without inhibitor, *i*_{corr}, and its value in the presence

Table 1

Corrosion parameters of Pb after 60 min of the electrode immersion in acidic solutions, pH 2 using different amino acids at a constant concentration of 0.025 M at 25 °C

	E_{corr} (mV)	R_{corr} ($\text{k}\Omega \text{cm}^2$)	i_{corr} ($\mu\text{A}/\text{cm}^2$)	β_a (mV/dec)	β_c (mV/dec)	Corrosion rate ($\mu\text{m}/\text{Y}$)	η (%)
pH 2	-510.6	0.274	60.68	77.7	-107.6	1.8×10^6	-
Glycine	-518.7	0.349	55.32	74.2	-221.4	1.6×10^6	8.83
Alanine	-516.6	0.349	43.90	69.8	-110.7	1.3×10^6	27.65
Valine	-520.8	0.324	47.89	73.8	-109.9	1.4×10^6	21.08
Histidine	-525.5	0.246	44.33	43.9	-65.2	1.3×10^6	26.94
Glutamic	-519.1	0.342	31.64	53.0	-118.8	0.94×10^6	47.90
Cysteine	-526.4	0.078	98.30	44.4	-65.5	2.92×10^6	-ve

Table 2

Corrosion parameters of Pb after 60 min of the electrode immersion in neutral solutions, pH 7 using different amino acids at a constant concentration of 0.025 M at 25 °C

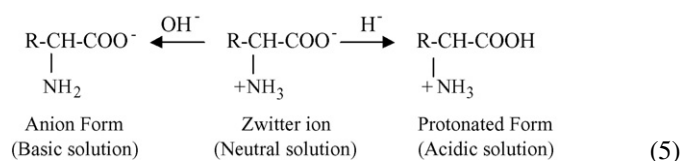
	E_{corr} (mV)	R_{corr} ($\text{k}\Omega \text{cm}^2$)	i_{corr} ($\mu\text{A}/\text{cm}^2$)	β_a (mV/dec)	β_c (mV/dec)	Corrosion rate ($\mu\text{m}/\text{Y}$)	η (%)
pH 7	-455.3	4.040	4.69	119.4	-78.2	139.40	-
Glycine	-458.8	5.490	2.95	105.2	-58.4	86.07	37.20
Alanine	-483.9	8.030	1.39	69.5	-60.3	40.53	70.40
Valine	-429.2	3.520	2.54	53.3	-62.8	75.34	45.96
Histidine	-462.5	3.290	3.02	62.6	-93.5	89.59	35.70
Glutamic	-531.8	17.620	0.49	58.3	-41.4	14.53	87.67
Cysteine	-719.3	0.511	9.95	51.0	-80.4	0.295×10^6	-ve

of the inhibitor, $i_{\text{corr(inh)}}$, according to:

$$\eta = \frac{i_{\text{corr}} - i_{\text{corr(inh)}}}{i_{\text{corr}}} \times 100 \quad (4)$$

The calculated values of the Pb corrosion inhibition efficiency with the different amino acids in the acidic, neutral and basic solutions are also included in the same tables. The values of η show that the effect of the inhibitor depends on two factors, its molecular structure and the electronic structures of both the inhibitor and the metal [18,19]. The inhibition efficiency increases with an increased chain length of the amino acid due to the ability to cover larger surface area, so alanine has higher inhibition efficiency than glycine. The degree of chain branching appears to have the opposite effect to the chain length. The chain branching prevents the dense packing of the adsorbed layer, thus reducing the effect of protection, so valine is less protective than alanine. In the case of glutamic acid, the corrosion inhibition efficiency increases up to 87% in neutral solutions. This can be attributed to the fact that glutamic acid is a large molecule, its coverage ability will be more than the other investigated amino acids and hence it gives higher inhibition efficiency. The corro-

sion inhibition process is based on the adsorption of the amino acid molecules on the active sites of the metal surface [20]. In neutral solutions, the amino acid molecules are presented usually as Zwitter ions in the form:



In neutral and acidic solutions, the amino acid molecule is adsorbed through the +NH_3 on the electrode surface (cathodic regions of the local corrosion cell) and decrease the rate of the cathodic reaction, thus the rate of the anodic reaction (dissolution process) will be decreased. In basic solutions, the presence of the amino acids shifts the value of E_{corr} to more positive values (-693.5 to -612.6 mV) with a decrease in the anodic current density, i.e. the amino acid acts as anodic inhibitor, where it is adsorbed on the metal surface, blocking the active sites for the corrosion process, thus decreasing the exposed free metal area to corrosive medium.

Table 3

Corrosion parameters of Pb after 60 min of the electrode immersion in basic solutions, pH 12 using different amino acids at a constant concentration of 0.025 M at 25 °C

	E_{corr} (mV)	R_{corr} ($\text{k}\Omega \text{cm}^2$)	i_{corr} ($\mu\text{A}/\text{cm}^2$)	β_a (mV/dec)	β_c (mV/dec)	Corrosion rate ($\mu\text{m}/\text{Y}$)	η (%)
pH 12	-693.5	0.962	15.94	116.1	-78.6	473.2	-
Glycine	-669.6	1.090	12.43	94.1	-75.8	362.8	21.99
Alanine	-665.0	1.120	11.82	95.8	-75.4	345.0	25.8
Valine	-679.2	1.060	13.93	98.9	-75.8	406.4	12.6
Histidine	-670.0	1.360	8.06	74.8	-80.9	235.1	49.4
Glutamic	-612.6	2.030	6.11	88.3	-70.1	178.3	61.6
Cysteine	-900.7	1.020	6.73	29.2	-60.7	199.7	57.8

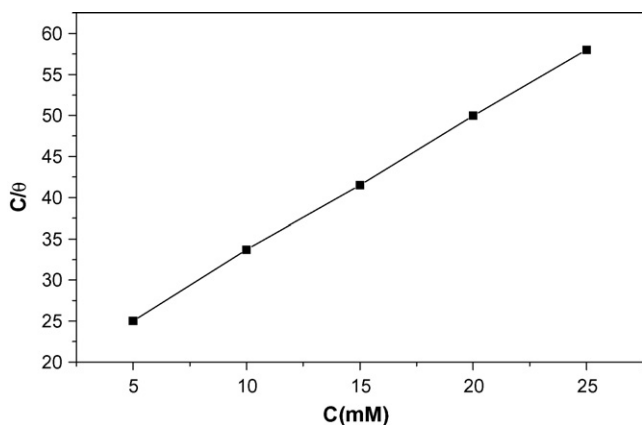


Fig. 4. Adsorption isotherm for the adsorption of glutamic acid on Pb in neutral solutions at 25 °C.

3.3. The adsorption isotherm

To obtain more information about the interaction between the amino acid molecules and the electrode surface, different adsorption isotherms were investigated. The degree of surface coverage, θ , at different concentrations of the amino acids in neutral solutions was calculated from the corresponding electrochemical polarization measurements according to [21]:

$$\theta = \frac{i_{\text{corr}} - i_{\text{corr(inh)}}}{i_{\text{corr}}} \quad (6)$$

The obtained values of θ were fitted to different isotherms including Langmuir, Frumkin, Temkin, etc. The Langmuir isotherm, Eq. (7), was verified in the case of glutamic acid, which is based on the assumption that all adsorption sites are equivalent and that particle binding occurs independently from nearby sites being occupied or not [22].

$$KC = \frac{\theta}{1 - \theta} \quad (7)$$

where C is the concentration of the inhibitor, θ the fractional surface coverage and K is the adsorption equilibrium constant. The value of K is related to the free energy of adsorption ΔG_{ads} as [22,23]:

$$K = \frac{1}{C_{\text{solvent}}} \exp\left(\frac{-\Delta G_{\text{ads}}}{RT}\right) \quad (8)$$

where C_{solvent} represents the molar concentration of the solvent which is 55.5 mol/dm³ in the case of water, R the universal gas constant and T is the temperature. The Langmuir adsorption isotherm can be rearranged to obtain the following mathematical formulation:

$$\frac{C}{\theta} = \frac{1}{K} + C \quad (9)$$

A linear relationship can be obtained on plotting C/θ as a function of C , with a slope of unity, and the value of the intercept is the reciprocal of K . The results of the adsorption of glutamic acid on Pb in neutral solutions are presented in Fig. 4, the expected linear relationship is obtained and the value of the free energy of adsorption of glutamic acid on Pb, ΔG_{ads} , was calculated to

be -2.9 kJ/mol. A value of -40 kJ/mol is usually adopted as a threshold value between chemi- and physisorption [24]. The calculated value for the adsorption of glutamic acid on Pb electrode indicates that adsorption is of a physical nature, and there is no chemical interaction between the inhibitor molecule and the metal surface.

3.4. The electrochemical impedance measurements

The results of the potentiodynamic polarization experiments were confirmed by impedance measurements, since the electrochemical impedance spectroscopy (EIS), is a powerful technique in studying corrosion mechanisms and adsorption phenomena [25]. The experimental impedance results are simulated to pure electronic models that can verify or rule out mechanistic models and enables the calculation of numerical values corresponding to the physical and/or chemical properties of the electrochemical system under investigation [26–28]. The effect of the presence of the different amino acids on the corrosion behavior of Pb electrode in aqueous acidic, neutral and basic solutions was investigated. The Bode plots for Pb electrode in amino acid free and then in the presence of alanine, glutamic or histidines in aqueous solutions of different pH are presented in Fig. 5a–c for the acidic, neutral and basic solutions, respectively. Similar Bode plots are obtained for Pb in presence of other amino acids, glycine, valine and cysteine (not shown). Bode plots are recommended as standard impedance plots, since all experimental impedance data are equally represented and the phase angle, as a sensitive parameter to interfacial phenomena, appears explicitly [25,26]. The phase maximum at the intermediate frequencies broadens in the presence of the amino acid, which indicates the presence of passivation phenomenon [29]. The impedance data were analyzed using software provided with the electrochemical workstation, where the dispersion formula was used. In this formula an empirical factor α ($0 \leq \alpha \leq 1$) is introduced to account for the deviation from the ideal capacitive behavior due to surface inhomogeneities, roughness factors and adsorption effects [26–29]. The experimental values are correlated to the simple equivalent circuit model (Randles model) presented in Fig. 6. The calculated equivalent circuit parameters for Pb in absence and presence of the different amino acids in acidic, neutral and basic solutions are presented in Tables 4–6, respectively. Generally, the Bode plots show a single phase maximum at intermediate frequencies, which indicates the presence of one time

Table 4
Equivalent circuit parameters of Pb after 60 min of the electrode immersion in acidic solutions, pH 2 using different amino acids at a constant concentration of 0.025 M at 25 °C

	R_s ($\Omega \text{ cm}^2$)	R_{corr} ($\text{k}\Omega \text{ cm}^2$)	C_{dl} ($\mu\text{F}/\text{cm}^2$)	α
pH 2	27.6	0.09819	22.69	0.993
Glycine	32.49	0.09736	16.34	0.993
Alanine	31.02	0.1011	15.70	0.992
Valine	32.07	0.1273	12.49	0.992
Histidine	31.83	0.1233	12.90	0.993
Glutamic	31.36	0.1241	32.05	0.993
Cysteine	31.44	0.01431	12.45	0.901

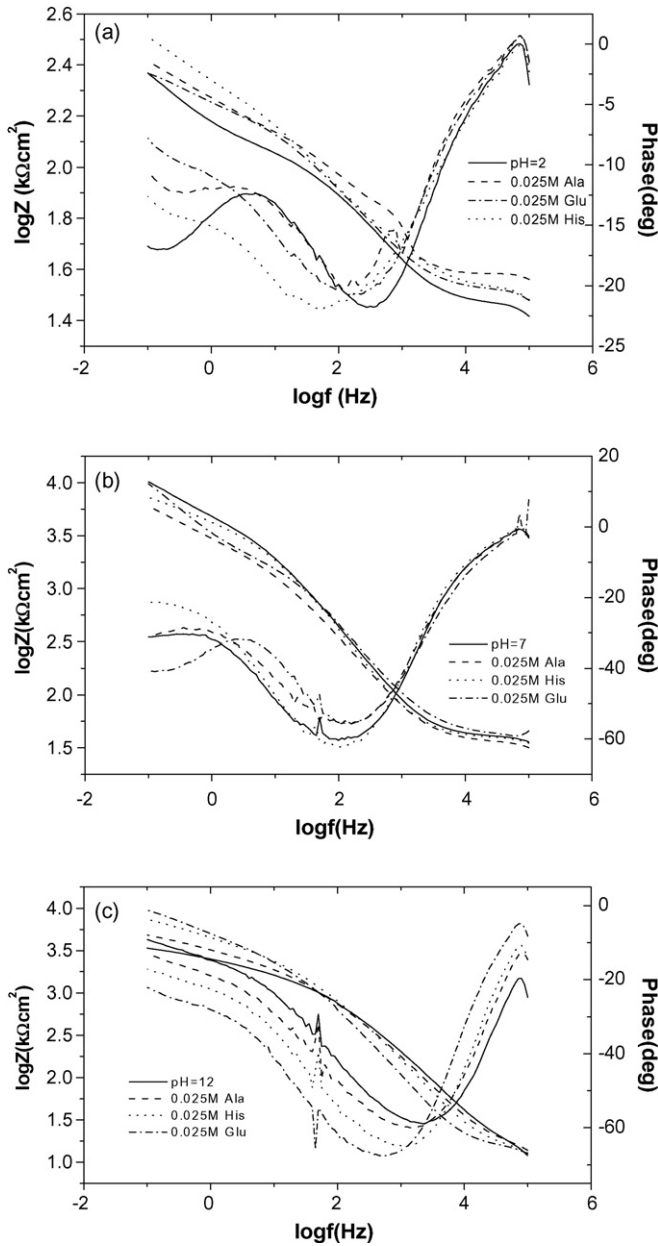


Fig. 5. Bode plots for Pb after 60 min of the electrode immersion in aqueous solutions of different pHs using different amino acids at 25 °C: (a) pH 2, (b) pH 7 and (c) pH 12.

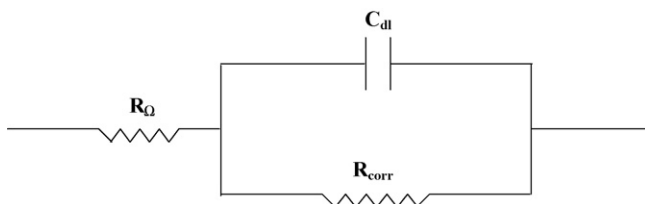


Fig. 6. Equivalent circuit model for a simple electrochemical cell (Randles model).

Table 5

Equivalent circuit parameters of Pb after 60 min of the electrode immersion in neutral solutions, pH 7 using different amino acids at a constant concentration of 0.025 M at 25 °C

	R_s (Ω cm ²)	R_{corr} (k Ω cm ²)	C_{dl} (μ F/cm ²)	α
pH 7	40.15	2.793	18.00	0.993
Glycine	32.01	2.804	5.67	0.999
Alanine	32.90	5.168	5.48	0.999
Valine	26.23	6.723	4.21	0.999
Histidine	34.71	4.270	6.63	0.999
Glutamic	55.53	4.425	2.27	0.923
Cysteine	28.30	0.0691	8.12×10^3	0.994

Table 6

Equivalent circuit parameters of Pb after 60 min of the electrode immersion in basic solutions, pH 12 using different amino acids at a constant concentration of 0.025 M at 25 °C

	R_s (Ω cm ²)	R_{corr} (k Ω cm ²)	C_{dl} (μ F/cm ²)	α
pH 12	12.62	1.242	40.47	0.999
Glycine	13.44	1.294	38.84	1
Alanine	14.18	1.422	35.36	1
Valine	9.57	1.397	34.74	0.999
Histidine	13.40	1.540	32.64	0.999
Glutamic	14.28	1.482	33.92	0.998
Cysteine	12.78	0.559	56.98	0.999

constant representing the electrode process. The values of the corrosion resistance, R_{corr} , and the thickness of the passive film, $1/C_{dl}$ [30,31], increase in the presence of the amino acids, which can be attributed to the adsorption of the amino acid molecules on the electrode surface. The increase of R_{corr} and $1/C_{dl}$ is remarkable in both the neutral and basic solutions and glutamic acid shows the highest value of $1/C_{dl}$ indicating a strong adsorption on the active sites of the electrode surface, and the formation of thicker adsorption layer.

4. Conclusions

Amino acids, especially glutamic acid show promising inhibition efficiency for the corrosion of Pb in neutral and basic solutions. The mechanism of the corrosion inhibition process is based on the adsorption of the amino acid molecule on the metal surface. The lead corrosion inhibition efficiency of the investigated amino acids in neutral solutions follows the order:

Glutamic acid > alanine > valine > glycine > histidine
> cysteine

The adsorption of glutamic acid on Pb follows the Langmuir adsorption isotherm and the free energy of adsorption in neutral solutions amounts to -2.9 kJ/mol, indicating the physical adsorption of the amino acid molecules on the metal surface.

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