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The inhibition effect of some amino acids towards the corrosion of aluminum in 1 M HCl + 1 M H_2SO_4 solution

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Abstract

The inhibition effect of some amino acids towards the corrosion of aluminum in 1 M HCl + 1 M H_2SO_4 solution was investigated using weight loss measurement, linear polarization and SEM techniques. The results drawn from the different techniques are comparable. The used amino acids were alanine, leucine, valine, proline, methionine, and tryptophan. The effect of inhibitor concentration and temperature against inhibitor action was investigated. It was found that these amino acids act as good inhibitors for the corrosion of aluminum in 1 M HCl + 1 M H_2SO_4 solution. Increasing inhibitor concentration increases the inhibition efficiency and with increasing temperature the inhibition efficiency decreases. It was found that adsorption of used amino acids on aluminum surface follows Langmuir and Frumkin isotherms.

Keywords: Corrosion; Inhibitor; Amino acid; Mixed acidic media; Aluminum

1. Introduction

Aluminum has a remarkable economic and industrial importance owing to its low cost, light weight, high thermal and electrical conductivity. The most important feature in aluminum is its corrosion resistance due to the formation of a protective film on its surface upon its exposure to atmosphere or water. Anodizing in sulfuric acid solution can produce this protective layer [1]. The presence of chloride ions in the solution has some disadvantages like producing pitting in oxide film [2]. The protection of aluminum and its oxide films against the corrosive action of chloride ions has been extensively investigated and a great number of inhibitors have been studied [2–5]. Previous study showed that the addition of chloride ions to sulfate solutions enhances aluminum corrosion [6]. Also without concerning this problem, the inhibition of aluminum corrosion in acidic solutions was extensively studied using organic and inorganic compounds [7–16]. Unfortunately many common corrosion inhibitors are health hazards. To solve this problem, some researchers were investigated the

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inhibition effect of amino acids on corrosion of metals [17–26].

The focus of this study is to investigate the inhibition properties of some amino acids in mixed acidic media to evaluate their inhibition effect in a strong acidic media containing de-passivator chloride ions. These inhibitors are nontoxic relatively cheap and easy to produce in purities greater than 99%. Weight loss measurements and polarization methods were used to determine the inhibition efficiency of these amino acids.

2. Experimental method

2.1. Linear polarization

Aluminum metal with purity of 99.99% provided by Merck was used in this study. For polarization studies, the specimens were mounted in polyester in such a way that only 1 cm^2 surface area was in contact with the corrosive media. The 2 cm × 2 cm plastic molds, containing liquid polyester, catalyze and hardener (all from TABA CHEMIE Company, Iran), were used to mount the aluminum samples. The samples become hard after 24 h in the room temperature. Mounted samples were polished with emery papers grade 280 for removing the polyester from the aluminum surface. The aluminum surface in mount was polished with different grades of emery papers 400, 600, 800, 1000, and 1200. Afterwards, the polished aluminum was immersed in 1 M NaOH aqueous solutions at 80 °C for 1.5 min, degreased with acetone and rinsed by double distilled water [27].

Platinum and a saturated calomel (SCE) electrode were used as auxiliary and reference electrodes, respectively. The samples were first immersed into the solution for 1 h to establish a steady state open circuit potential. Galvanostat–potentiosat Autolab (PGSTAT20) apparatus was used as a potential source that connected to a PC S-Pentium computer. All the corrosion data are obtained from polarization curves using GPES (Version 4.5) software. After measuring the open circuit potential between sample electrode and reference electrode, the potential scan carried out at 2 mV s^{-1}. Each polarization was run three times and corrosion potentials and corrosion currents were reproducible within ±5 mV and ±1 μA cm^{-2}. The effect of acid concentration on aluminum corrosion was determined by measuring corrosion rate in different concentration of acids, and for the evaluation of inhibitor concentration effects on the protection of corrosion, the experiments were carried out in 1 M HCl + 1 M H_2SO_4 in the absence and presence of various concentrations of inhibitors. The effect of temperature on corrosion inhibition of amino acids was investigated at three different temperatures. Distilled water was used to prepare solutions. All used chemicals were of reagent grade.

2.2. Weight loss measurements and SEM technique

Aluminum sheets with double side's surface area of 2.925 cm^2 were used for weight loss measurements. These were bent into a U form, immersed in 1 M NaOH aqueous solution at 80 °C for 2 min, degreased with acetone, rinsed with distilled water, dried, weighted and introduced into the test solutions with their edges downward. A new test piece was used for each experiment. The measurements were carried out in different temperatures and in different concentrations of inhibitors. The sheets obtained from weight loss measurements are used in SEM studies.

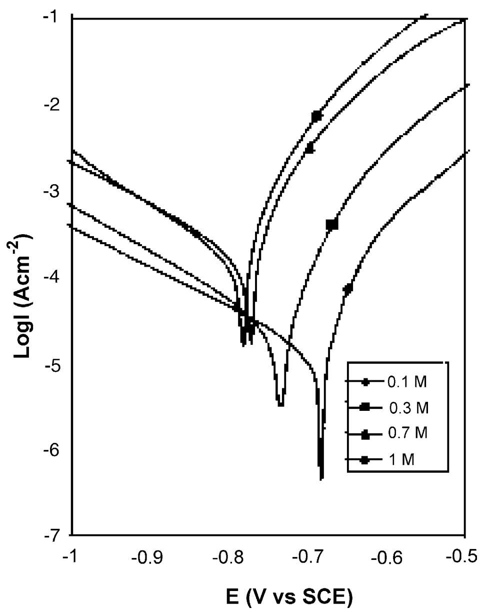

Fig. 1. Effect of acid concentration on aluminum polarization curves.

Table 1
Polarization parameter of aluminum corrosion in different acid concentration

Concentration (M)	R_p (Ω cm^2)	E_{corr} (V)	Corrosion rate (mm per year)
0.1	152	−0.680	0.19
0.3	136	−0.734	0.27
0.7	131	−0.772	1.94
1	120	−0.782	2.07

3. Results and discussion

3.1. Linear polarization

Fig. 1 shows the effect of acid concentration on polarization curves of aluminum and corresponding corrosion data are given in Table 1. The data in Table 1 reveal that with increasing acid concentration, corrosion rate increases. This behavior has two reasons increasing hydrogen ion reduction in cathodic

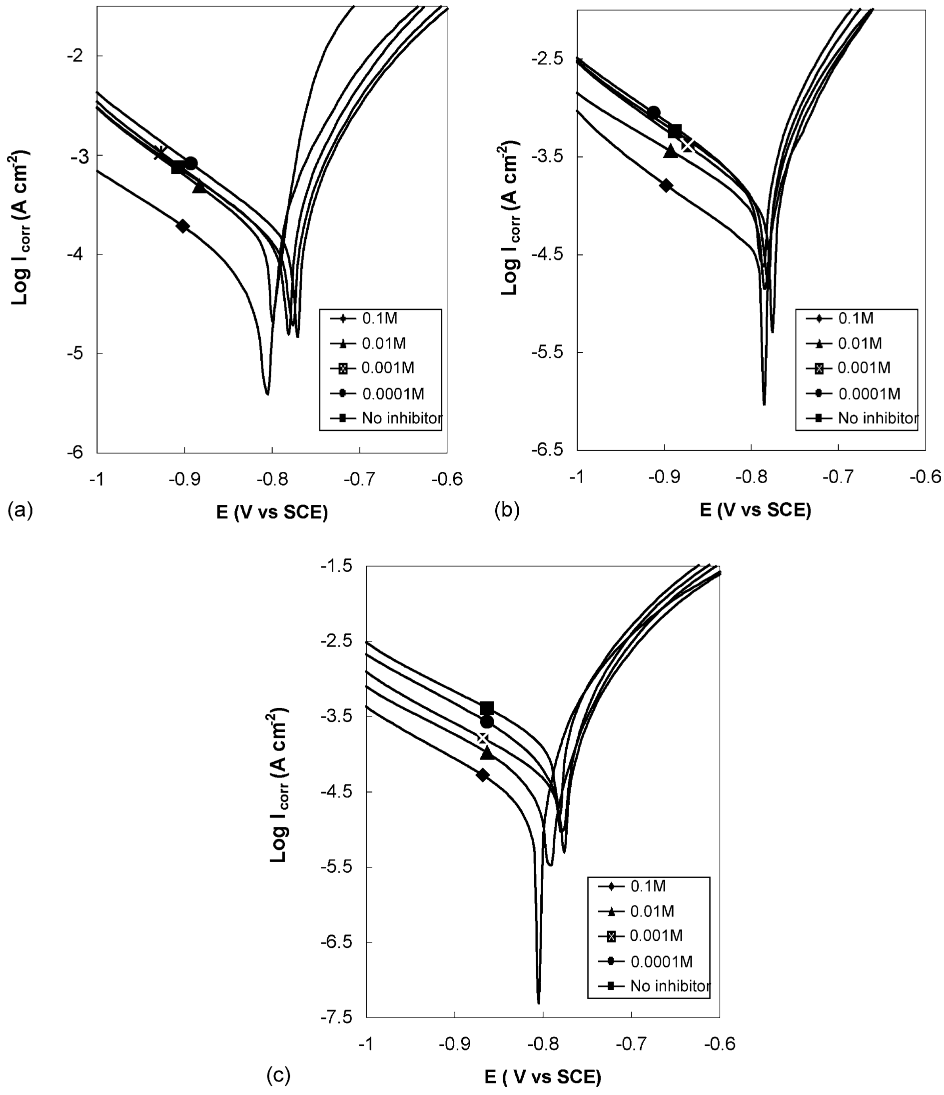

Fig. 2. Effect of amino acid concentration on aluminum polarization curves in 1 M HCl + 1 M H_2SO_4: (a) alanine, (b) leucine, (c) methionine.

Table 2
Corrosion data for aluminum in mixed acid solution in the presence of different concentrations of amino acid obtained from linear polarization method

Inhibitor	Inhibitor concentration	E_{corr} (V)	R_p (Ω cm^2)	Corrosion rate (mm per year)
Alanine	0.1	−0.806	201	0.90
	0.01	−0.798	142	1.77
	0.001	−0.777	135	1.81
	0.0001	−0.772	120	1.96
Valine	0.1	−0.793	262	0.85
	0.01	−0.766	143	1.61
	0.001	−0.764	113	1.90
	0.0001	−0.783	102	1.95
Leucine	0.1	−0.786	297	0.77
	0.01	−0.782	179	1.39
	0.001	−0.776	156	1.48
	0.0001	−0.787	112	1.92
Methionine	0.1	−0.802	570	0.39
	0.01	−0.792	439	0.41
	0.001	−0.777	325	0.64
	0.0001	−0.777	201	1.00
Proline	0.1	−0.801	298	0.75
	0.01	−0.781	287	0.99
	0.001	−0.772	133	1.89
	0.0001	−0.762	104	1.98
Tryptophan	0.1	−0.806	816	0.22
	0.01	−0.811	469	0.46
	0.001	−0.812	399	0.54
	0.0001	−0.830	141	1.45

area and increasing chloride and sulfate ions concentration, which increase aluminum dissolution [5,6]. Fig. 2 shows the effect of inhibitor concentration on the polarization curves of aluminum corrosion. All amino acids show relatively same behavior against the polarization and so we show only the first three amino acids polarization curves in all studies. Corrosion parameters in the 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). In the case of alanine and proline, with increasing inhibitor concentration, E_{corr} shifts to more negative values and it indicates that these inhibitors have been adsorbed to cathodic areas and act as cathodic inhibitors. In the case of leucine and valine in concentrations higher than 10^{-4} M these inhibitors act as an anodic inhibitor. In the case of

Table 3
Inhibition efficiencies of amino acids on aluminum corrosion in 1 M HCl + 1 M H_2SO_4 at 25 °C obtained from polarization measurements

Amino acid	Concentration (M)			
	0.1	0.01	0.001	0.0001
Alanine	56.3	14.3	12.1	4.8
Valine	58.2	21.7	7.4	5.3
Leucine	62.4	32.8	28.0	6.9
Proline	63.3	51.9	8.5	4.8
Methionine	81.0	79.9	68.6	51.3
Tryptophan	90.0	77.5	64.3	29.6

methionine in concentrations lower than 10^{-2} M E_{corr} is constant and both of cathodic and anodic reactions are influenced but in concentrations higher than 10^{-2} M, E_{corr} shifts to negative values and this inhibitor act as a cathodic inhibitor. With increasing concentration, tryptophan acts as an anodic inhibitor and in this case with increasing concentration E_{corr} shifts to positive values. The following equation was used to calculate inhibition efficiency (IE) from polarization measurements:

$$\text{IE} = (1 - i/i_0) \times 100$$

where i and i_0 are the corrosion current densities (A cm^{-2}) obtained by extrapolation of the cathodic and anodic Tafel lines, in inhibited and uninhibited solutions, respectively. The inhibition efficiencies of inhibitors are given in Table 3. The inhibition efficiency of 0.1 M amino acids at 25 °C is in the order: tryptophan > methionine > proline > leucine > valine > alanine.

It seems that the chemical adsorption has a fundamental role to coverage the cored sites respect to physical adsorption. Although, in this concentration, amine group can protonated, but the presence of indole, pyrrole, or S–CH_3 group on the amino acids, decreases the stability of positive charge on the amino acids. However, it is well known that the presence of aromatic ring, hetero atoms, or long chain aliphatic groups on the inhibitor structure causes a significant increase in inhibition efficiencies. Electron in aromatic ring and electron pairs on the hetero atoms can be shared to aluminum orbitals forming insoluble complex that protect the surface from the aggressive ions.

Among the studied amino acids, tryptophan exhibits the best inhibition efficiency respect to the

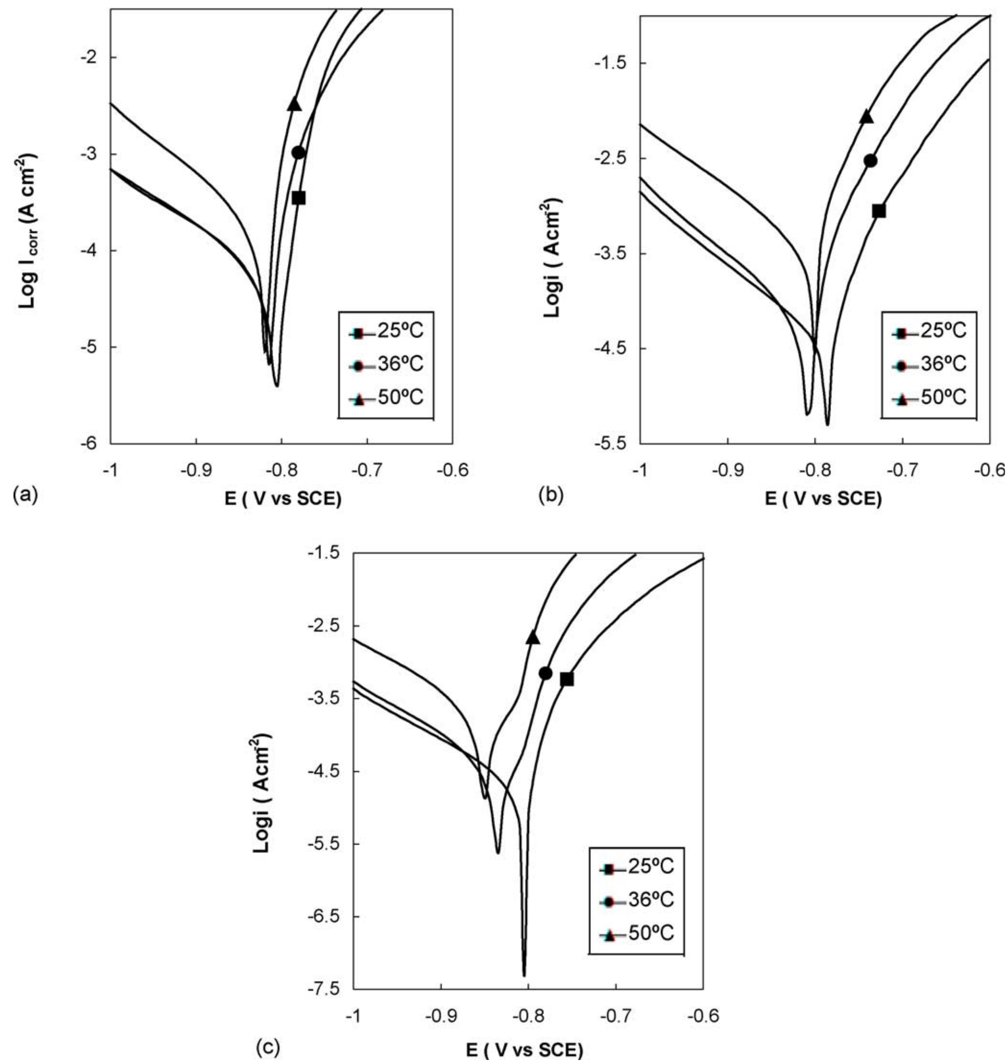

Fig. 3. Effect of temperature on aluminum polarization curves in the presence of 0.1 M of amino acids: (a) alanine, (b) leucine, (c) methionine.

others, probably because of the excess nitrogen atoms and the presence of aromatic ring in molecule, which can increases the adsorption of molecules on aluminum surface. Another possibility is that, since tryptophan is a large molecule, its coverage ability will be more than others. In the case of methionine, sulfur atom in aliphatic chain can increases the interaction of molecule with metal surface. Proline with nitrogen atom in aliphatic ring can increases interaction with aluminum due to inductive negative charge property. In the cases of alanine, leucine and valine with non-polar hydrocarbon side chain on a carbon, when the functional group becomes larger, the inhibition increases. It can be deduced that the structure of the side chains significantly affects the inhibition efficiencies.

Fig. 3 shows the effect of temperature on the polarization curves of aluminum. In the presence of all amino acids, with increasing temperature, polarization resistance decreases, corrosion current and therefore corrosion rate increases (Table 4). It can be seen that in the case of alanine, methionine, proline and valine,

Table 4
The effect of temperature on the corrosion parameters of aluminum in the presence of 0.1 M of inhibitors

Inhibitor	Temperature (°C)	E_{corr} (V)	R_p (Ω cm^2)	Corrosion rate (mm per year)
Alanine	25	−0.806	201	0.90
	36	−0.811	203	1.04
	50	−0.816	54	3.93
Leucine	25	−0.786	297	0.77
	36	−0.806	200	1.00
	50	−0.800	43	4.73
Methionine	25	−0.802	570	0.39
	36	−0.822	303	0.61
	50	−0.851	36	1.73
Proline	25	−0.801	298	0.75
	36	−0.802	132	1.48
	50	−0.820	36	5.80
Tryptophan	25	−0.806	816	0.22
	36	−0.817	341	0.51
	50	−0.806	28	8.13
Valine	25	−0.793	262	0.85
	36	−0.807	218	0.92
	50	−0.809	43	1.54

with increasing the temperature E_{corr} shifts to more negative values and it indicates that these inhibitors influence cathodic areas. In the case of leucine and tryptophan with increasing temperature up to 36 °C, E_{corr} shifts to negative values and at 50 °C they act as anodic inhibitors.

3.2. Weight loss measurement

The weight loss of aluminum sheets (with 2.925 cm^2 surface area) in 1 M HCl + 1 M H_2SO_4 in the absence and the presence of used amino acids were determined after 3 h immersion time in different temperatures. In all cases, increasing the inhibitor concentration increases the inhibition efficiency. These results show that the dissolution of aluminum increases with temperature. Therefore the adsorption

Table 5
Inhibition efficiencies of amino acids on aluminum corrosion in 1 M HCl + 1 M H_2SO_4 at 25 °C obtained from weight loss measurements after 3 h

Amino acid	Concentration (M)			
	0.1	0.01	0.001	0.0001
Alanine	64.2	50.8	24.2	13.2
Valine	67.5	61.2	55.8	32.0
Leucine	68.3	64.4	57.3	39.2
Proline	87.7	75.5	69.9	62.2
Methionine	91.2	82.4	76.3	68.6
Tryptophan	93.0	91.2	87.8	87.7

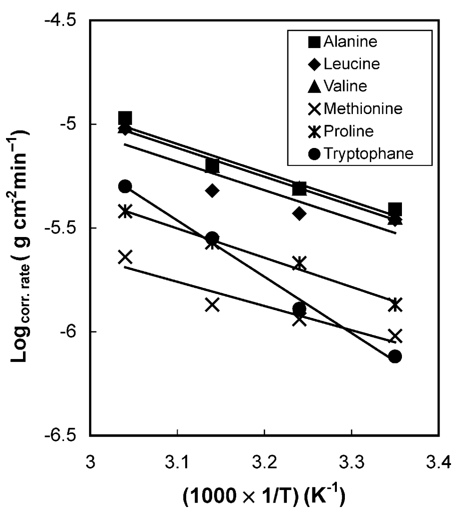

Fig. 4. Curves based on Arrhenius equation to calculate the activation energy of corrosion reaction.

Table 6
Activation energies of the corrosion of aluminum in 1 M HCl + 1 M H_2SO_4 in the presence of the inhibitors

Inhibitor	E_a (kJ mol^{-1})
Alanine	26.45
Valine	26.53
Leucine	26.82
Proline	27.01
Methionine	29.61
Tryptophan	50.55

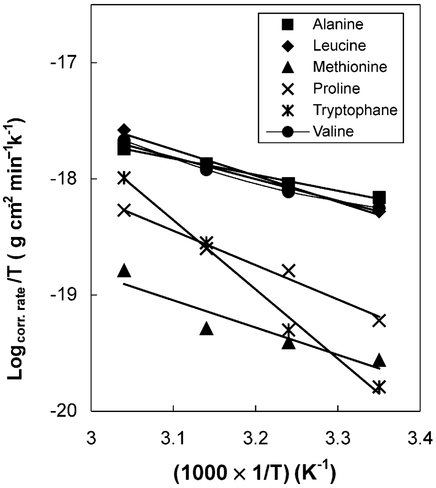

Fig. 5. Transition state equation plots of the corrosion reaction in the presence of amino acids.

of amino acids decreases. The inhibition efficiencies of the additives are calculated according to [6]:

$$\eta\,(\%) = \frac{W_{\text{free}} - W_{\text{add}}}{W_{\text{free}}} \times 100$$

where W_{free} and W_{add} are the weight losses of Al due to the dissolution in 1 M HCl + 1 M H_2SO_4 in the absence and presence of different concentration of inhibitor respectively. The inhibition efficiency of inhibitors is given in Table 5. It can be seen that,

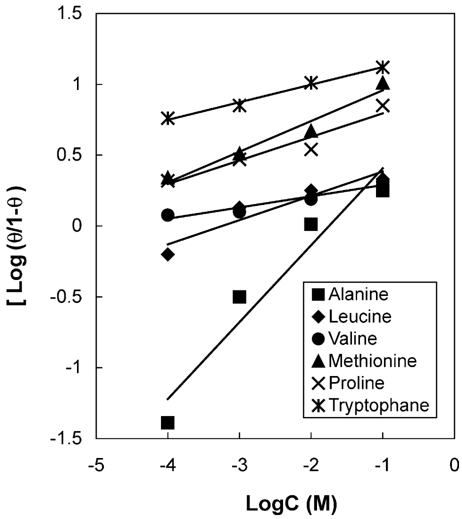

Fig. 6. Curves fitting of amino acids adsorption by Langmuir isotherm.

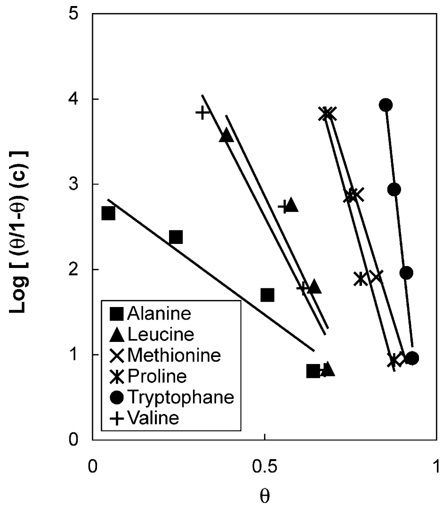

Fig. 7. Curves fitting of amino acids adsorption by Frumkin isotherm.

Table 7
Thermodynamic parameters for corrosion of aluminum in 1 M HCl + 1 M H_2SO_4 in presence of different amino acids

	Inhibitor					
	Alanine	Valine	Leucine	Proline	Methionine	Tryptophan
ΔH° (kJ mol^{-1})	11.52	23.85	22.74	35.54	24.51	46.92
ΔS° (J K^{-1} mol^{-1})	−309.86	−269.44	−274.61	−247.29	−278.90	−205.52

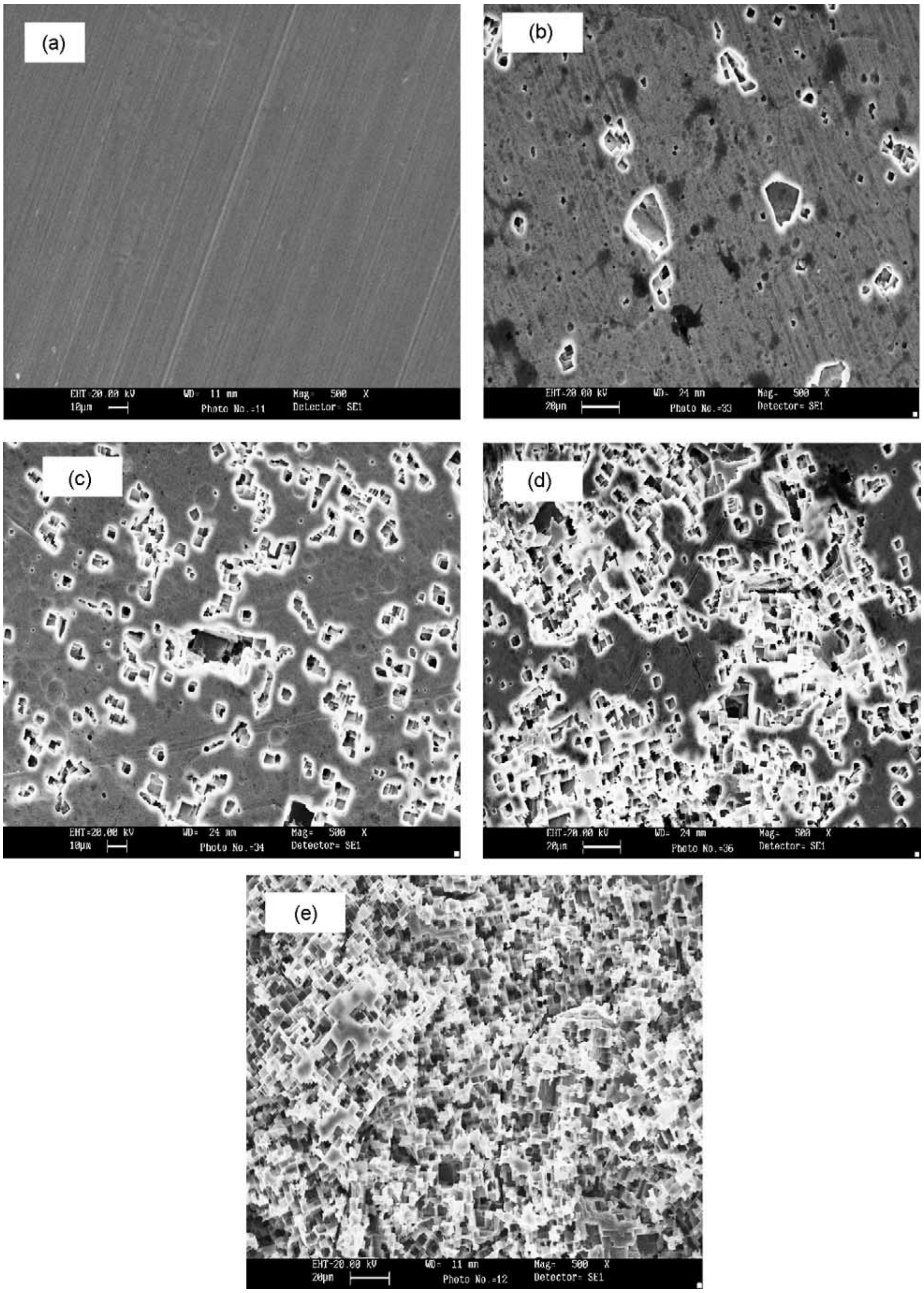

Fig. 8. SEM images of aluminum surface before corrosion and after immersion in different concentration of mixed acid medias: (a) before corrosion, (b) 0.3 M, (c) 0.5 M, (d) 0.7 M, (e) 1 M.

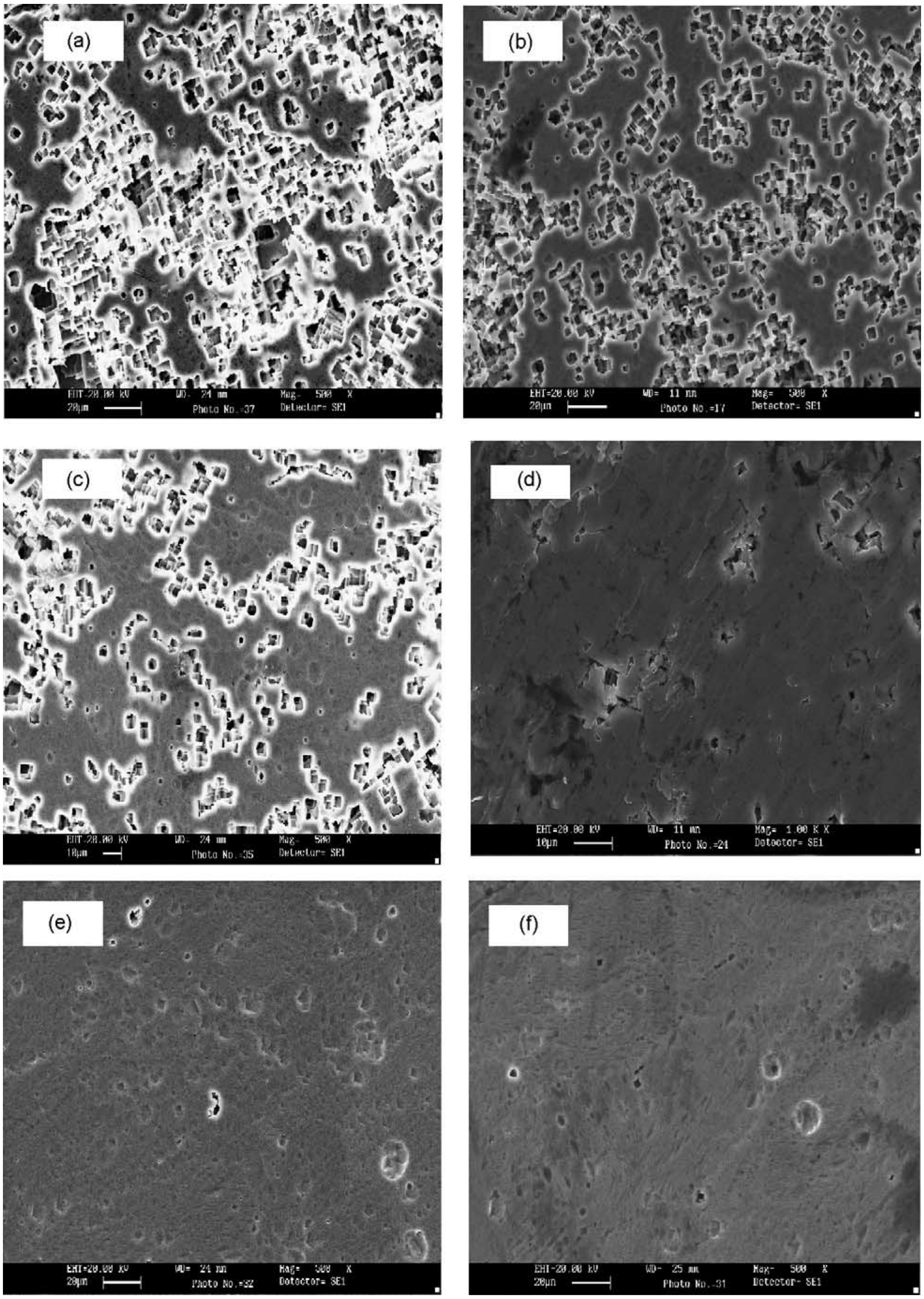

Fig. 9. SEM images of aluminum surface after immersion in mixed acid media 1 M HCl + 1 M H_2SO_4 in the presence of amino acids (0.1 M) after 3 h at 25 °C: (a) alanine, (b) valine, (c) leucine, (d) proline, (e) methionine, (f) tryptophan.

the weight loss of aluminum depends on both the type and concentration of additives.

The activation energy and thermodynamic parameters (E_a, ΔH° and ΔS°) for the corrosion reaction of Al in 1 M HCl + 1 M H_2SO_4 in the absence and presence of different concentration of these inhibitors were calculated from Arrhenius-type equation [6]:

$$k = A\,e^{-E_a/RT}$$

and transition-state equation [6]:

$$k = RT(e^{\Delta S^\circ/R}\,e^{-\Delta H^\circ/RT})/Nh$$

where E_a is the apparent activation energy, R the ideal gas constant, h the Planck's constant, N the Avogadro's number, ΔH° and ΔS° the thermodynamic functions. A plot of log(corrosion rate) for Al obtained from weight loss measurements as a function of $1/T$ gives straight lines (Fig. 4) with a slope of $-E_a/2.303R$.

The activation energies of the corrosion reaction in the presence of these inhibitors were determined and are given in Table 6. The activation energies of the inhibited corrosion reaction are relatively small, indicating that a physical adsorption takes place in the first stage. This behavior is due to an increase in surface area of metal covered by inhibitor. By using the transition state equation, a plot of log(corrosion rate/T) against ($1/T$) gives straight lines as shown in Fig. 5. From the intercept and slops of these lines we can calculate the entropy and enthalpy, which their values are given in Table 7. The values reflect the exothermic behavior of these inhibitors on the Al surface. The large negative values of ΔS° indicate that, the inhibition process is primarily enthalpy controlled.

The θ values are calculate from corrosion data of Al in 1 M HCl + 1 M H_2SO_4 with different additives to study the adsorption phenomena by adsorption isotherms [6]:

(a) Langmuir isotherm:

$$\log\frac{\theta}{1-\theta} = \log b + \log C$$

where θ is the surface coverage function, k the equilibrium constant of the adsorption reaction and C the inhibitor concentration in the bulk of the solution. The equation is the ideal equation that should be applied to the ideal case of physical or chemical adsorption on a smooth surface with no interaction between adsorbed molecules. Fig. 6 gives the results of plot for corrosion inhibition data of these compounds.

(b) Frumkin isotherm:

$$\ln\left(\frac{\theta}{1-\theta}[C]\right) = \ln k + 2\alpha\theta$$

where α is the lateral interaction term describing the molecular interaction in the adsorbed layer. The positive value of α indicates the attractive behavior of inhibitors. This relation gives a straight line, and therefore Frumkin isotherm is applicable as in Fig. 7. The differences between the slopes indicate the different attraction between inhibitors.

3.3. SEM techniques

Fig. 8 shows the aluminum surface before corrosion and after immersion in different concentration of mixed acid media. Images show that with increasing acid concentration, corrosive surface area increases. Fig. 9 shows the aluminum surface after immersion in mixed acid media in the presence of amino acids (0.1 M) after 3 h at 25 °C. With increasing inhibition efficiency, covered surface increases and dissolution of aluminum decreases.

4. Conclusion

Amino acids show good corrosion inhibition property against aluminum corrosion in the mixed acid media. Inhibition efficiencies are related to concentration, temperature and chemical structure of amino acids. Generally amino acids inhibition efficiencies increase when the concentration increases and temperature decreases. Presence of aromatic ring and hetero atoms such as sulfur and nitrogen on the amino acid structure causes a significant increase in inhibition efficiency. All amino acids affected both anodic and cathodic reactions, so they are classified as mixed type inhibitor. Adsorption of these inhibitors on the aluminum surface obeys from Langmuir and Frumkin isotherms. The SEM images confirm the protection of aluminum corrosion in mixed acids solutions by amino acids.

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