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Inhibition Efficiency of Some Amino Acids in the Presence of Vanillin for the Corrosion of Mild Steel in HCl Solution

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The inhibition of corrosion of mild steel in HCl in the presence of vanillin (van) coexisting with some amino acids, *i.e.*, valine (val), cysteine (cys), methylcysteine hydrochloride (m-cys) and methionine (meth) are compared. The possible synergistic inhibition of the corrosion by these amino acids using vanillin are also examined. It has been found that the inhibition efficiency of the studied amino acids in HCl is arranged as follows; meth < m-cys < *cys* < val. In the presence of vanillin, the inhibition efficiencies are arranged as follows; m-cys < val < meth < cys. This arrangement of the inhibition efficiency is explained based on the possible synergistic adsorption of the studied amino acids with the pre-adsorbed chloride ions.

Keywords: Adsorption, Eco-friendly corrosion inhibitor, Synergism, Adsorption, Amino acids

1. INTRODUCTION

Deterioration of materials due to corrosion waste resources, decrease productivity and damage environment [1-3]. The production efficiency and life time of the equipment in addition to products poisoning are another examples of the bad impact of the formation of scale as a result of corrosion. Using acids to remove undesirable scales and corrosion products is one of the remedial solutions [1-3]. However, acids should be mixed with corrosion inhibitors to reduce the further dissolution of metals in such harsh media. Utilizing organic inhibitors has been a subject of interest for long time [4-6]. The inhibition efficiency of these inhibitors are inherently related to the presence of at least one functional group (reaction center) which acts as a center for the adsorption process [4-6].

Recently many organic inhibitors has been reported as toxic and thus much interest has been paid to finding an eco-friendly corrosion inhibitors [7-16]. On the other hand enhancing the adsorption of organic inhibitors with anions and/or cations on the surface of the corroded metal via the synergistic adsorption have been extensively studied [17-22]. Such enhanced adsorption often accessed via a co-operative adsorption of the different species resulting in an increasing of the surface concentration of the organic inhibitors [23]. Just joint adsorption might result in what is the so called synergism; a process which may largely enhance the corrosion inhibition efficiency and even convert a corrosion promoter to a corrosion inhibitor.

However, all those studies concern with a variety of compounds that may fulfill some properties and lack others. For instance, some synthetic compounds even though they are an efficient inhibitors, but are not eco-friendly and their large inhibition efficiency is overweighed by the bad impact on the environment. Their damage is to the extent to disturb a biochemical process or an enzyme system at some site in the body [24]. Recently, investigations have been directed to study naturally occurring substances in order to find low-cost and non-hazardous corrosion inhibitors. In the present study the corrosion inhibition of some amino acids as an eco-friendly compounds in the presence of another benign compounds, i.e., vanillin is studied. Synergism save much money as large inhibition efficiency is achieved using low concentration of an inhibitor with the help of cheap coexisting species [25, 26].

2. EXPERIMENTAL

2.1. Mild Steel Sample

Mild steel samples subjected to corrosion studies are of composition (wt. %): 0.07% C, 0.29% Mn, 0.07% Si, 0.012% S, 0.021% P and the remainder iron. Samples of geometric area 0.5 cm^2 were used.

2.2. Inhibitor

Chemicals were obtained from Sigma-Aldrich and used as received. Solutions of HCl were prepared by dilution of AR grade of their stock solutions. Stock solutions of examined inhibitors, either vanillin and/or selected amino acids, i.e., valine (val), cysteine (cys), methylcysteine hydrochloride (m-cys) and methionine (meth) were prepared in 1M HCl and the desired concentrations were obtained by appropriate dilution.

2.4. Electrochemical Measurements

Electrochemical experiments were conducted in a conventional three-electrode cell with a platinum counter electrode (CE) and a $Hg/Hg_2SO_4/SO_4^{2-}$ coupled to a fine Luggin capillary as the reference electrode (RE). The Luggin capillary was kept close enough to the working electrode (WE) to minimize the ohmic contribution. The results are presented versus calomel electrode.

The WE surface area of 0.5 cm^2 was polished with emery paper down to 2000 on test face, rinsed with distilled water, degreased with acetone, and dried with a cold air stream. Before measurements the electrode open circuit potential (OCP) was recorded at 25 ^{o}C until the steady state is obtained. All electrochemical measurements were carried out using PGSTAT30 potentiostat/galvanostat. The potential of potentiodynamic polarization curves was conducted from a potential of *ca*. -150 mV vs. OCP, to 150 mV vs. OCP at a scan rate of 2 mV/s. Current densities were calculated on the basis of the apparent geometrical surface area of the electrode.

3. RESULTS AND DISCUSSION

3.1. Effect of concentration of vanillin

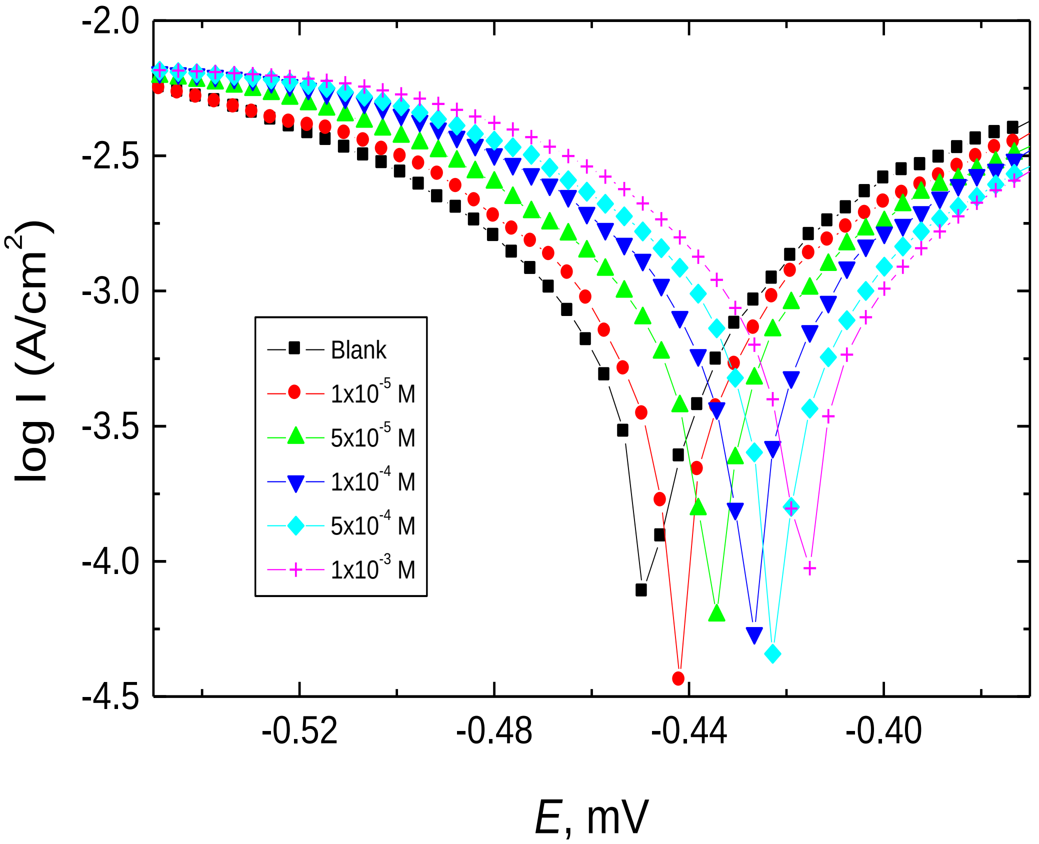

Figure 1. Tafel plots obtained at mild steel in 1.0 M HCl solution in the absence and presence of different concentrations of vanillin at 25 ^{o}C.

Figure 1 shows the Tafel plots obtained at mild steel in 1.0 M HCl in the absence and presence of various concentrations of vanillin at 25 ^{o}C. Electrochemical parameters extracted from this figure are given in Table 1.

As can be seen the corrosion potential is shifted positively. This is reflected in a considerable suppressing of the anodic current in the presence of vanillin as compared with the blank response. On the other hand the cathodic current is enhanced in the presence of vanillin. The increase in the cathodic current is regular with the increase in the vanillin concentration. This behavior is completely different compared with the reported behavior in sulfuric acid in which the effect on the cathodic branch is considerable, while the effect on the anodic branch is negligible [27]. The large effect on the anodic branch in the present case might be attributed to the pre-adsorption of chloride ion during andodic scanning. During anodic scanning the potential is positive with respect to the potential of zero charge of iron. In other words, the positively charged electrode enhances the adsorption of chloride ions. Consequently, the adsorption of vanillin (pKa = 7.4 [28]) is enhanced and the anodic branch is suppressed. In the present case, the maximum shift in the corrosion potential is around 37 mV (obtained in the presence of 1 mM vanillin) revealing that the present inhibitor has a preferential effect on the anodic process. The overall effect is a quiet acceptable protection efficiency obtained at little high concentration of vanillin (ca. 79 at 1 mM vanillin). The protection efficiency is given by [29]:

$$\% P = \left[1 - \frac{i_{corr1}}{i_{corr2}}\right] 100 \qquad (1)$$

where, i_{cor1} and i_{cor2} are corrosion current densities in the absence and presence of inhibitor, respectively. Values of the protection efficiencies obtained in the presence of different concentrations are given in Table 1.

Table 1. Electrochemical parameters obtained at mild steel in 1.0 M HCl solution in the absence and presence of different concentrations of vanillin at 25 ^{o}C. Data were extracted from Fig. 1

[van], M	E_{corr} (mV)	β_c (mV/dec)	β_a (mV/dec)	I_{corr} (μA/cm^2)	% P
0	-452	97	79	2240	-
1x10^{-5}	-445	109	73	1782	20
5x10^{-5}	-436	118	66	1411	37
1x10^{-4}	-428	127	62	1120	50
5x10^{-4}	-423	135	59	795	64
1x10^{-3}	-415	144	56	486	79

Next the inhibition efficiency both in the individual presence of vanillin and valine and in their coexistence are examined and shown in Figure 2. The coexistence of valine with vanillin results in an increasing of the inhibition efficiency from 0.5 in the presence of 0.1 mM Vanillin to 0.78 in the presence of vanillin and valine, 0.1 mM each. Adding valine to vanillin enhances the inhibition of the anodic current and overweight that of the cathodic current. However, the summation of the inhibition efficiency in their individual presence is little bit smaller compared with the obtained inhibition efficiency in their coexistence denoting to the absence of a real synergistic effect.

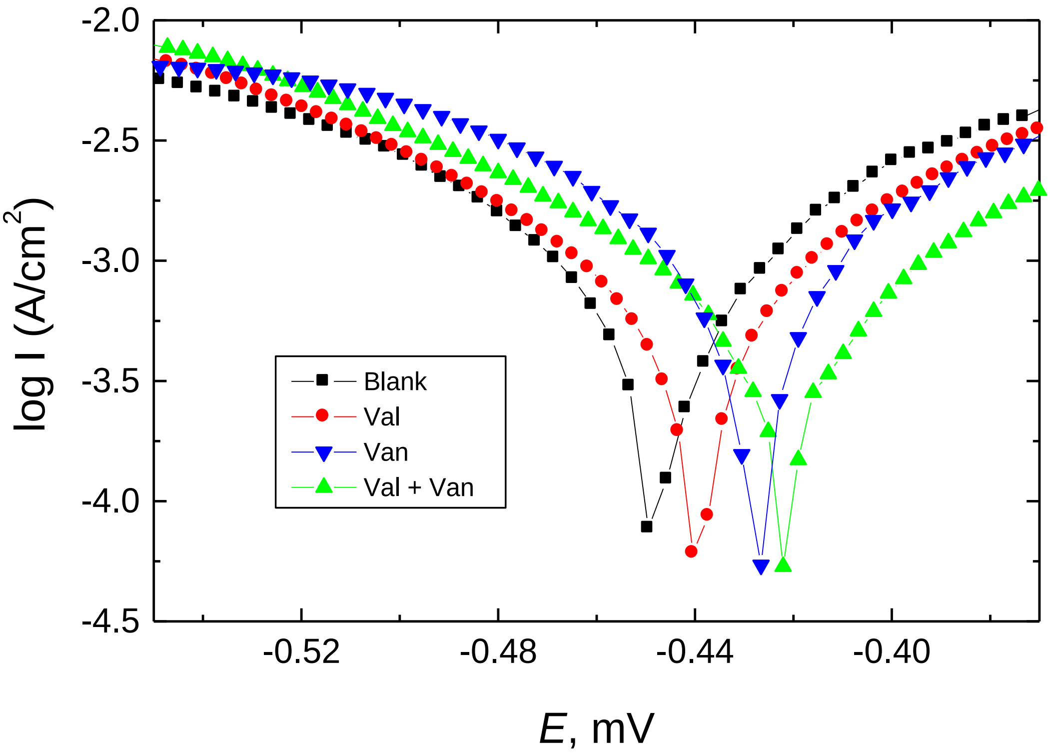

Figure 2. Tafel plots obtained at mild steel in 1.0 M HCl solution in the absence and presence of valine, vanillin and their mixture with concentrations of 1.0×10^{-4} M, each, at 25 ^{o}C.

Table 2. Electrochemical parameters obtained at mild steel in 1.0 M HCl solution in the absence and presence of valine, vanillin and their mixture with concentrations of 1.0×10^{-4} M at 25 ^{o}C. Data were extracted from Fig. 2.

Medium	E_{corr} (mV)	β_c (mV/dec)	β_a (mV/dec)	I_{corr} (µA/cm^2)	% *P*
Blank	-452	83	79	2240	-
Valine	-439	91	77	1413	37
Vanillin	-428	97	62	1120	50
Mixture	-421	106	55	501	78

Similar results were obtained in the coexistence of vanillin with either methionine, cysteine or methyl cysteine and results are given in figures 3-5 and Tables 3-5, respectively.

In the case of methionine (Fig. 3), there is a large decrease in the anodic current and at the same time the increase in the cathodic current obtained in the presence of vanillin is suppressed upon adding methionine, suppression in the case of methionine is larger than that obtained in the case of valine. This results in a real synergistic effect (the synergism parameter is larger than one), i.e., the protection efficiency in the presence of vanillin and methionine coexisting together is little bit larger than that calculated from the mathematical summation of the inhibition efficiencies obtained in their individual presences. Synergism means that the inhibition efficiency obtained in the coexisting of two or more species is larger than that obtained by the summation of their exerted inhibition efficiencies in their individual presence. The synergism parameter is given by Eq. 2 [30];

$$S_\theta = \left[\frac{1-\theta_{1+2}}{1-\theta'_{1+2}}\right]100 \qquad (2)$$

where $\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1\theta_2)$; θ_1 and θ_2 are the surface coverage in the individual presence of the vanillin and cysteine, respectively, and θ_{1+2} is the degree of the surface coverage in their coexistence. S_θ values give an indication about the simultaneous adsorption of the coexisting species while it is synergistic or antagonistic. S_θ values larger than one indicates a real synergism, and values smaller than one points to antagonism. In the present case both cathodic and anodic Tafel slopes obtained in the coexistence of the two species are comparable to that obtained in the their absence indicating an inhibition via simple adsorption.

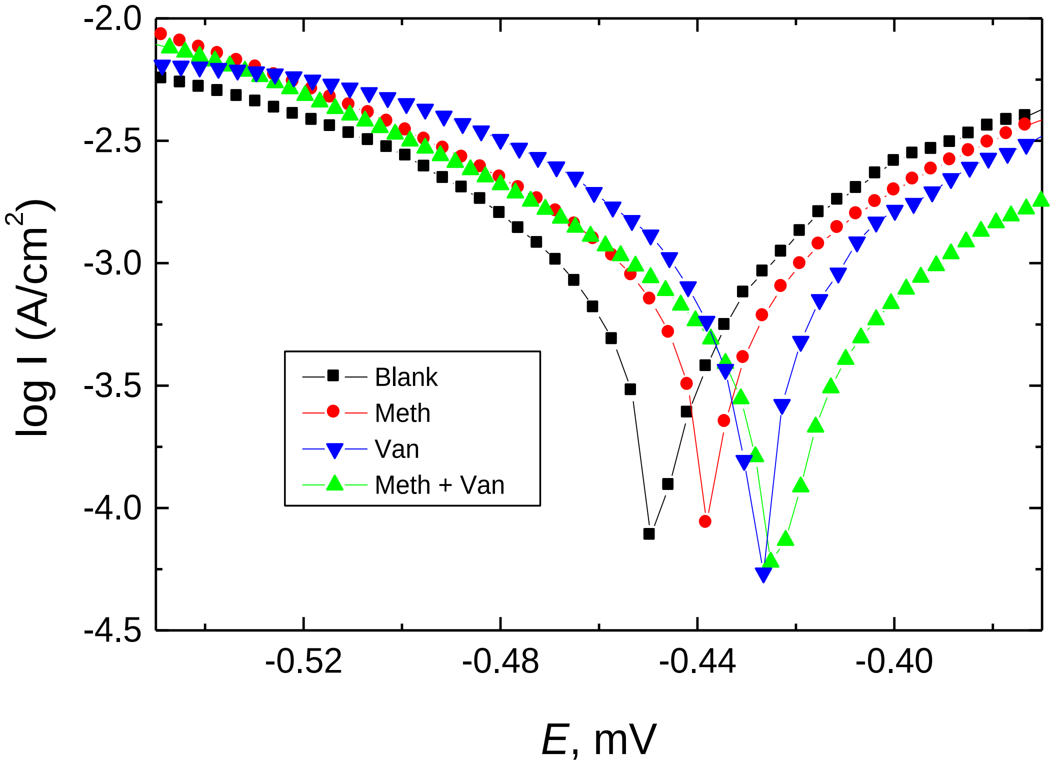

Figure 3. Tafel plots obtained at mild steel in 1.0 M HCl solution in the absence and presence of methionine, vanillin and their mixture with concentrations of $1.0\text{x}10^{-4}$ M at 25 ^{o}C.

Table 3. Electrochemical parameters obtained at mild steel in 1.0 M HCl solution in the absence and presence of methionine, vanillin and their mixture with concentrations of $1.0\text{x}10^{-4}$ M at 25 ^{o}C. Data were extracted from Fig. 3

Medium	E_{corr} (mV)	β_c (mV/dec)	β_a (mV/dec)	I_{corr} (μA/cm^2)	% *P*
Blank	-452	83	79	2240	-
Methionine	-438	87	77	1580	29
Vanillin	-428	97	62	1120	50
Mixture	-423	93	59	401	82

Results obtained in the presence of cysteine coexisting with vanillin are shown in Fig. 4. Data extracted from this figure are shown in Table 4. Suppressing of the cathodic branch is little larger than that obtained in the case of methionine, and this is reflected on the inhibition efficiency which is larger in the case of cysteine, and the synergism as well.

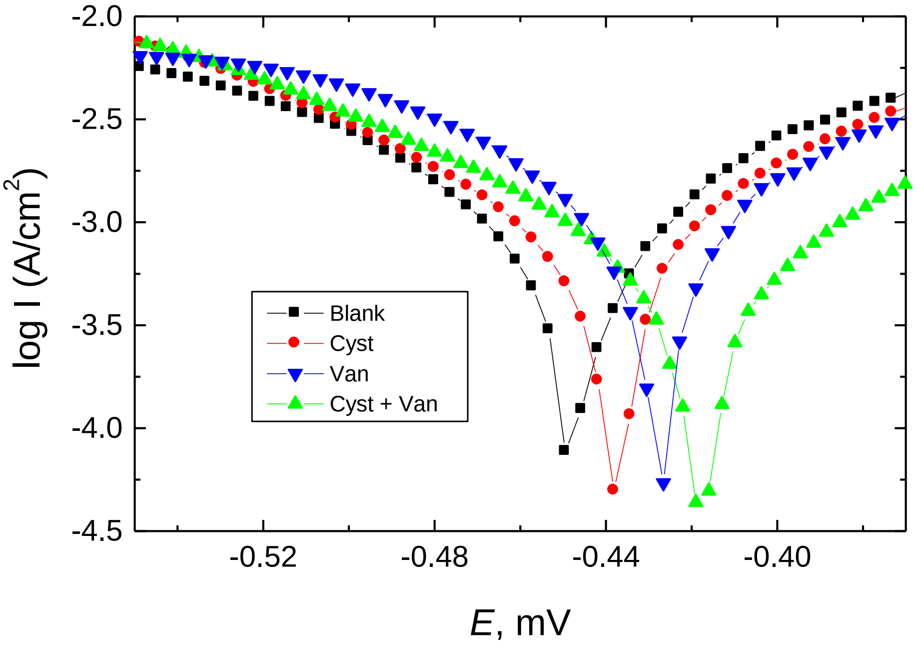

Figure 4. Tafel plots obtained at mild steel in 1.0 M HCl solution in the absence and presence of cysteine, vanillin and their mixture with concentrations of 1.0x10^{-4} M at 25 ^{o}C.

Table 4. Electrochemical parameters obtained at mild steel in 1.0 M HCl solution in the absence and presence of cysteine, vanillin and their mixture with concentrations of 1.0x10^{-4} M at 25 ^{o}C. Data were extracted from Fig. 4.

Medium	E_{corr} (mV)	β_c (mV/dec)	β_a (mV/dec)	I_{corr} (μA/cm^2)	% *P*
Blank	-452	83	79	2240	-
Cysteine	-442	85	74	1480	34
Vanillin	-428	97	62	1120	50
Mixture	-416	88	67	223	90

On the other hand when cysteine is replaced by methyl cysteine (see Fig. 5 and Table 5) the obtained inhibition efficiency is smaller compared with the previous mentioned amino acids, i.e. vanillin, cysteine and methionine. Also, adding the two species simultaneously does not reveal a real synergism.

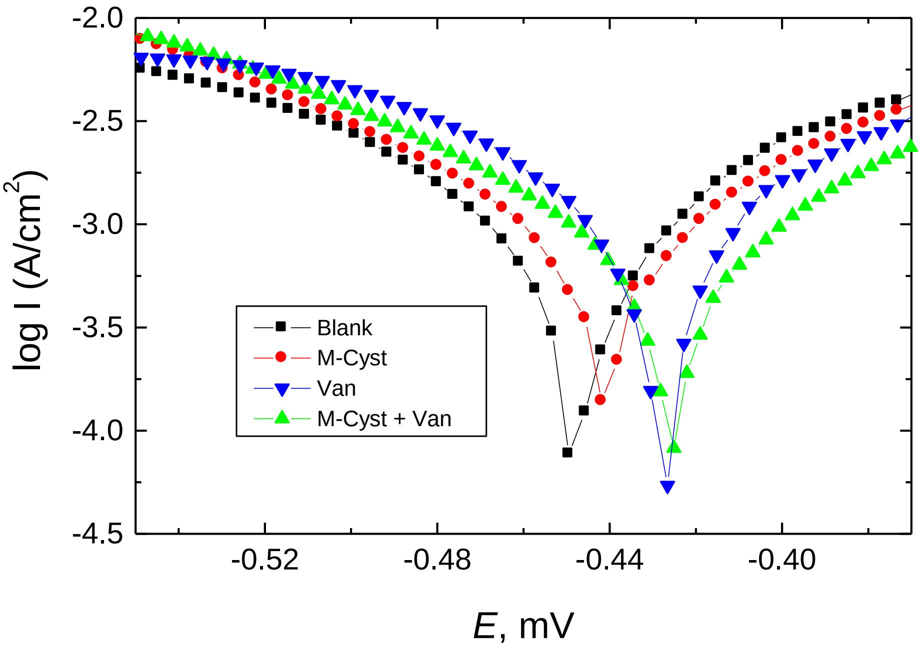

Figure 5. Tafel plots obtained at mild steel in 1.0 M HCl solution in the absence and presence of methyl cysteine, vanillin and their mixture with concentrations of 1.0x10^{-4} M at 25 ^{o}C.

Table 5. Electrochemical parameters obtained at mild steel in 1.0 M HCl solution in the absence and presence of methyl cysteine, vanillin and their mixture with concentrations of 1.0x10^{-4} M at 25 ^{o}C.

Medium	E_{corr} (mV)	β_c (mV/dec)	β_a (mV/dec)	I_{corr} (µA/cm^2)	% P
Blank	-452	83	79	2240	-
Methyl Cysteine	-445	112	81	1705	24
Vanillin	-428	97	62	1120	50
Mixture	-426	121	67	671	70

The inhibition efficiency in the presence of vanillin with studied amino acids is arranged as follows:

L-cysteine methyl ester hydrochloride < valine < methionine < cysteine

The largest inhibition efficiency obtained in the presence of vanillin and cysteine denotes to some co-operative interaction of both species on the metal surface. When cysteine is replaced by methyl cysteine the inhibition efficiency is largely decreased. This might be attributed to the replacement of the carboxylic group in the case of cysteine by the ester group in the methyl cysteine. Both cysteine and methionine showed larger inhibition efficiency compared with valine. This might be attributed to that both cysteine and methionine have thiol group, and this functional group impart extra ability for the adsorption on the iron surface.

4. CONSLUSIONS

The effect of some amino acids, both in the presence and absence of vanillin, on the corrosion of mild steel in hydrochloric acid solution has been studied. It has been found that the largest inhibition efficiency is obtained in the coexistence of vanillin and cysteine mixture. The inhibition efficiency in the presence of vanillin with studied amino acids is arranged as follows:

L-cysteine methyl ester hydrochloride < valine < methionine < cysteine

The inhibition efficiency of 90 % is obtained in the presence of vanillin and cysteine, 0.1 mM each.

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