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New Insight Into the Mechanism of the Inhibition of Corrosion of Mild Steel by Some Amino Acids

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The inhibition of the corrosion of mild steel in 0.5 M H_2SO_4 by vanillin in the presence of various amino acids, typically valine, methionine, cysteine and methylcysteine hydrochloride, are studied using potentiodynamic technique aiming at the elucidation of the mechanism of the corrosion inhibition. The corrosion inhibition of vanillin and amino acids was evaluated, both in their individual presence and in their coexistence. The largest inhibition efficiency has been found in the presence of vanillin and cysteine mixture. To have an insight into the mechanism of the inhibition and probe the adsorption sites of the inhibitor, the inhibition efficiency of a Schiff base, synthesized from vanillin and a selected amino acid, typically cysteine, has been compared with the inhibition efficiency of the vanillin and cysteine mixture. Interestingly, it has been found that the inhibition efficiency of the vanillin and cysteine mixture is much larger than the relevant Schiff base, and that the inhibition efficiency of the latter is much smaller than the inhibition efficiency in the presence of the individual components, i.e., vanillin and cysteine. This points to the blocking of the probable adsorption sites, upon the formation of Schiff base, which is the amino group of cysteine and the aldehydic group of vanillin. The adsorption of the methylcysteine, as an example, in the presence of vanillin was found to follow Temkin isotherm and that the chemical adsorption mode is controlling as revealed from the free energy of adsorption (44.4 kJ/mol).

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

1. INTRODUCTION

Metals and alloys are generally considered the corner blocks in many industrial applications. Metals are subjected to corrosion which is a serious problem in most industries. Mild steel is commonly used in wide applications in a broad spectrum of industries and machinery. It has a tendency to corrode especially in acid media that are frequently used in industry during cleaning, acid pickling, acid descaling and petrochemical processes [1].

The use of corrosion inhibitors is one of the remedial methods of protecting metals against corrosion [2]. The majority of well-known inhibitors are synthetic organic compounds containing hetero atoms in their aromatic or long carbon chain such as O, N or S, and multiple bonds, which allow an adsorption on the metal surface resulting in blocking the active sites on the alloy surface and, thereby, reduce the corrosion rate [3]. Even though, such synthetic compounds show good anticorrosive action, most of them are highly toxic to both human beings and environment [4-8]. Research on eco-friendly corrosion inhibition has been extensively increased in the last decade [9-22]. On the other hand several studies have been reported on the joint adsorption of organic inhibitors with anions and/or cations on the surface of corroded metal, what is the so-called synergism [23-27].

The present study is devoted for enhancing the corrosion inhibition exerted by some amino acids, as an-eco-friendly corrosion inhibitors, by another benign compound, typically vanillin. It also aims at elucidating the mechanism of adsorption of those amino acids and probing the active site for adsorption. The mechanism is elucidated by comparing the inhibitive action of vanillin and the studied amino acids both in the uncoupled case and in the coupled one, i.e., as Schiff base derived from vanillin and the nominated amino acid. Amino acids are characterized by eco-friendly properties, water solubility, naturally occurring and biodegradability [28]. Amino acids have been reported as efficient corrosion inhibitors for Cu, Al, Sn and iron, with inhibition action based on the nature of the metal and the corrosive medium [29-47]. It has been reported that amino acids containing sulphur and longer hydrocarbon chains shows significant inhibition effect [48]. The majority of the research on the corrosion inhibition by amino acids are directed to copper [49-51] and iron [52-60]. Regarding corrosion inhibition of iron by amino acids, the inhibition efficiency has been reported to depend inherently on the medium and the structure of amino acids, and the inhibition efficiency in some cases enhanced by adding some cations and anions [61-64].

2. EXPERIMENTAL

2.1. Mild Steel Sample

Electrochemical experiments were conducted on mild steel 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

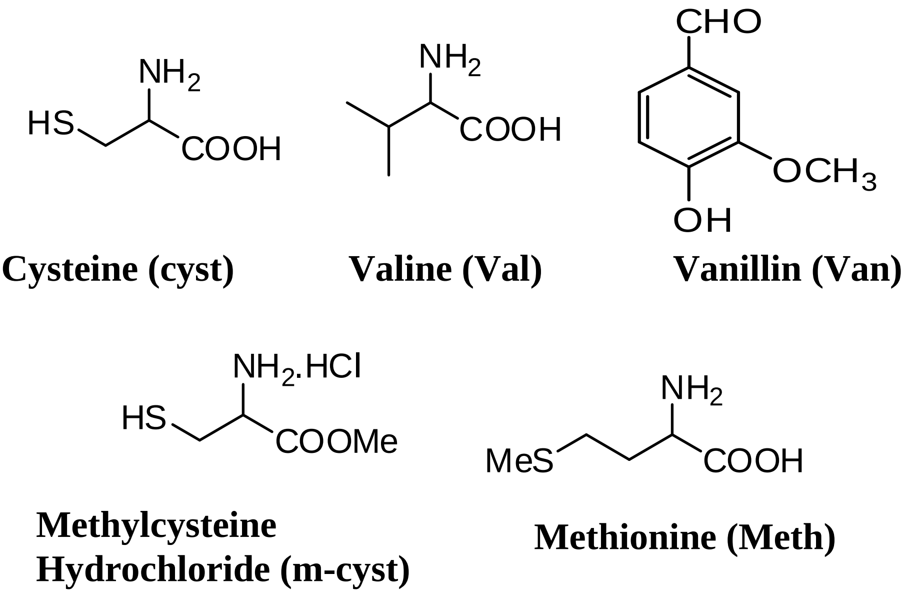
Vanillin and amino acids of structures shown below (Fig. 1) were obtained from Sigma-Aldrich and used as received. The Schiff base of amino acids and vanillin was prepared according to the reported procedures [65].

2.3. Solutions

The solution of 0.5 M H_2SO_4 was prepared by dilution of AR grade 98% H_2SO_4. Stock solutions of examined inhibitors, either vanillin and/or selected amino acids were prepared in 0.5 M H_2SO_4 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.



Cysteine (cyst) **Valine (Val)** **Vanillin (Van)**

Methylcysteine Hydrochloride (m-cyst) **Methionine (Meth)**

Figure 1. Structure of studied inhibitors

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 for 30 min at 25 ^oC or 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.

2.5. SEM measurements

Scanning electron microscopy (SEM) was carried out using a Hitachi microscope. An accelerating voltage of 20 kV was used for all of the imaging done in this work. Also, all images were taken at magnifications as 5μm.

2.6. Synthesis of Schiff base

The Schiff base of the amino acid or its methyl ester was synthesized by the condensation of 2-vanillin with selected amino acid in 1:1 molar ratio using anhydrous ethanol as the reaction medium. The solutions were refluxed on water bath for 9-10 hrs. and followed by thin layer chromatography until complete disappearing of the starting materials. The reaction mixture was allowed to cool at room temperature. The solid products were obtained and excess solvent was removed. Further, it was dried and then recrystallized from same solvent.

2.7. Characterization of synthesized Schiff base

The IR spectra give enough information to confirm the binding of the vanillin to the amino acid. The starting material i.e. amino acids shows strong absorption peaks at 3370 cm^{-1} and 3310 cm^{-1} which are characteristic peaks of NH_2 group. In the synthesized Schiff base, those two peaks completely dissapeared. In addition, a new sharp and strong peak is observed at 1628 cm^{-1} which is assigned for azomethine group (>C=N) (data are not shown), confirming the formation of azomethine compound.

3. RESULTS AND DISCUSSION

3.1. Effect of concentration of vanillin

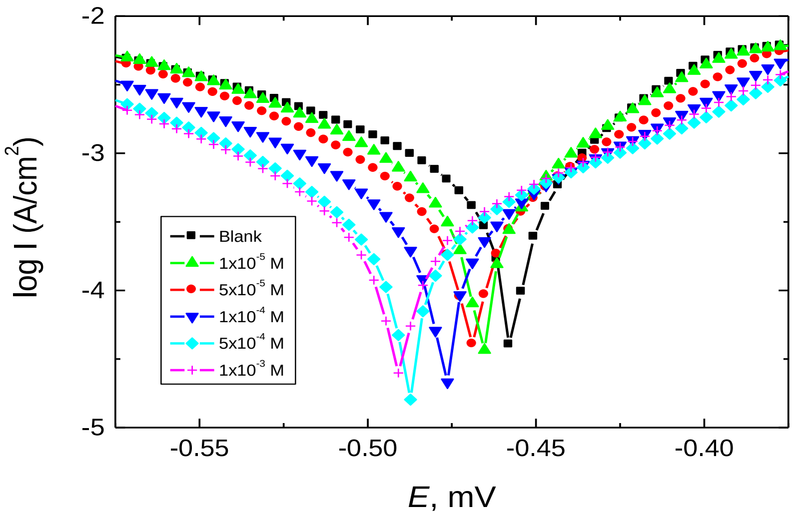


Figure 2. Potentiodynamic polarization curves for mild steel in 0.5 M H_2SO_4 in the absence and presence of different concentrations of vanillin (Van) at 25 ^oC.

Figure 2 shows the polarization curves of mild steel obtained in 0.5 M H_2SO_4 in the absence and presence of various concentrations of vanillin at 25 ^oC. Electrochemical parameters extracted from this figure are given in Table 1. As can be seen the effect of vanillin on the cathodic branch is significant compared with the effect on the anodic one; the cathodic branch bodily shifted to lower currents, i.e., vanillin preferentially inhibit the cathodic branch. Also the corrosion potential shifted to cathodic direction. However, the potential shift is smaller than 85 mV and thus the vanillin can be nominated as a mixed type inhibitor [66, 67]. It has been reported that the open circuit potential, E_{OCP}, displacement could be utilized as a diagnosis of the type of the inhibitor; if E_{OCP} is at least ± 85 mV different to the one measured in the blank solution it can be classified as an anodic or cathodic inhibitor [66, 67]. In the present case, the maximum shift is around 26 mV (obtained in the presence of 1.0 mM of vanillin) revealing that the present inhibitor acts as a mixed type inhibitor with a preferential restrain on the cathodic process.

Table 1. Polarization data for mild steel in 0.5 M H_2SO_4 in the absence and presence of various concentrations of vanillin (Van) at 25 ^oC. Data were extracted from Fig. 2.

[Van], M	E_{corr} (mV)	β_c (mV/dec)	β_a (mV/dec)	I_{corr} (μA/cm^2)	θ	% P
0	-458	112	50	630	--	--
$1x10^{-5}$	-465	100	57	562	0.11	11
$5x10^{-5}$	-471	94	66	511	0.19	19
$1x10^{-4}$	-477	92	74	370	0.41	41
$5x10^{-4}$	-489	81	85	269	0.58	58
$1x10^{-3}$	-491	87	91	251	0.60	60

The effect of the inhibitor concentration on the cathodic Tafel slopes is negligible indicating that the inhibitor exerts its action via simple blocking, and that the adsorption of the inhibitor does not change the mechanism [68]. The adsorbed molecules mechanically screen the coated part of the electrode and therefore protect it from the action of the corrosion medium. On the other hand, anodic Tafel slope increases with the increase in the concentration of vanillin, This increase in the anodic Tafel slope suggests the interposition of the vanillin into the charge transfer process for the anodic reaction [69].

The inhibition efficiency is given by:

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

where, i_{cor1} and i_{cor2} are corrosion current densities in the presence and absence of inhibitor, respectively. Values of the inhibition efficiencies obtained in the presence of different concentrations are given also in Table 1. The maximum inhibition efficiency (ca. 79 %) obtained in the presence of 1.0 mM Vanillin.

Figure 3 depicts the Tafel plots obtained in 0.5 M H_2SO_4 (blank) containing vanillin and vanillin with different amino acids, typically, valine, methionine, cysteine and methyl cysteine, 5 x 10^{-4} M each. Data extracted from this figure are given in Table 2.

Inspection of figure 3 and Table 2 reveals the following;

Compared with the corrosion potential in 0.5 M H_2SO_4, all inhibitors shifted the corrosion potential in the negative direction of potential; the maximum shift (ca. 39 mV) is obtained in the presence of vanillin + valine mixture. The shift points that inhibitors acts as mixed type inhibitors since the shift is less than 85 mV [66, 67].

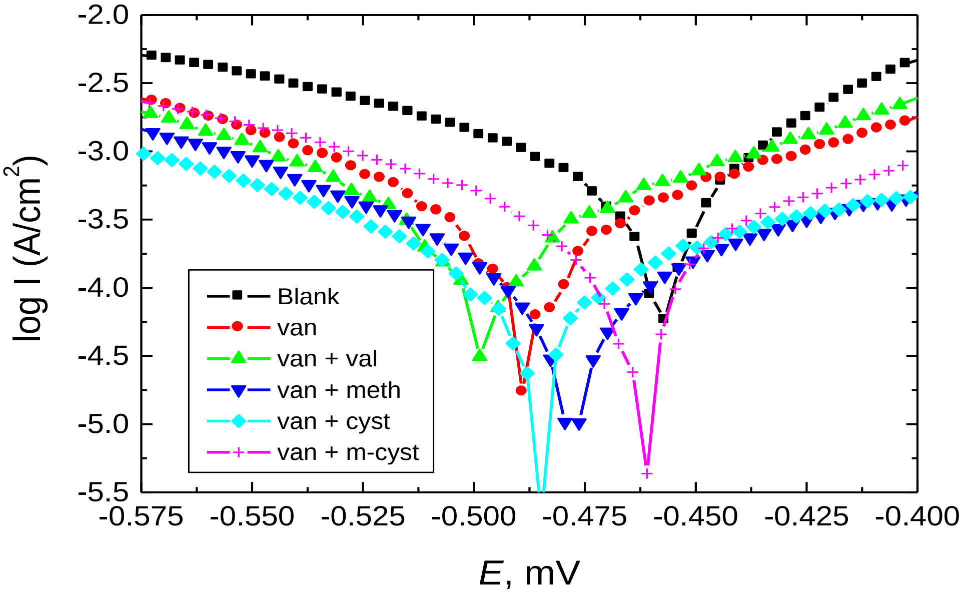


Figure 3. Potentiodynamic polarization curves for mild steel in 0.5 M H_2SO_4 in the absence and presence of $5x10^{-4}$ M vanillin (van) and amino acids, i.e, valin (val), methionine (meth), cysteine (cyst) and methyl cysteine (m-cyst) at 25 ^{o}C.

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

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

The largest inhibition efficiency obtained in the presence of vanillin and cysteine might be attributed to the interaction of both species on the metal surface. This point encourages us to try the preparation of Schiff bases derived from this amino acid and vanillin and study its corrosion inhibition behavior (see Fig. below). It is noteworthy to mention that the smallest inhibition efficiency is obtained in the coexisting of vanillin and valine (nitrogen-containing amino acid) compared with other amino acids which contains sulfur in the side chain. It has been reported that sulfur containing compounds are more efficient in inhibiting the corrosion of steel in H_2SO_4 solutions, while those containing nitrogen are efficient in HCl solutions [68].

Table 2. Polarization data for mild steel in 0.5 M H_2SO_4 in the absence and presence of mixture of vanillin (van) and studied amino acids (vanillin (van), methionine (meth), cysteine (cyst), methylcysteine (m-cyst)) at 25 ^oC. Data were extracted from Fig. **3.**

System	E_{corr} (mV)	β_c (mV/dec)	β_a (mV/dec)	I_{corr} (μA/cm^2)	θ	% P
Blank	-458	112	50	630	--	--
$5x10^{-4}$ M van	-489	91	85	269	0.58	58
$5x10^{-4}$ M van + $5x10^{-4}$ M val	-497	79	117	199	0.68	68
$5x10^{-4}$ M van + $5x10^{-4}$ M meth	-478	70	95	125	0.80	80
$5x10^{-4}$ M van + $5x10^{-4}$ M cyst	-485	83	114	79	0.87	87
$5x10^{-4}$ M van+$5x10^{-4}$ M m-cyst	-461	87	107	177	0.72	72

Figure 4 shows potentiodynamic polarization curves for mild steel in 0.5 M H_2SO_4 solution in the absence and presence of cysteine, vanillin and their mixture with concentrations of $1.0x10^{-4}$ M each at 25 ^oC. Results are compared with the Schiff base synthesized from vanillin and cysteine, according to the procedure cited in the experimental part, to tentatively probe the site of adsorption. Polarization parameters extracted from this figure are given in Table 3. Several interesting points can be extracted from Fig. 4 and Table 3.

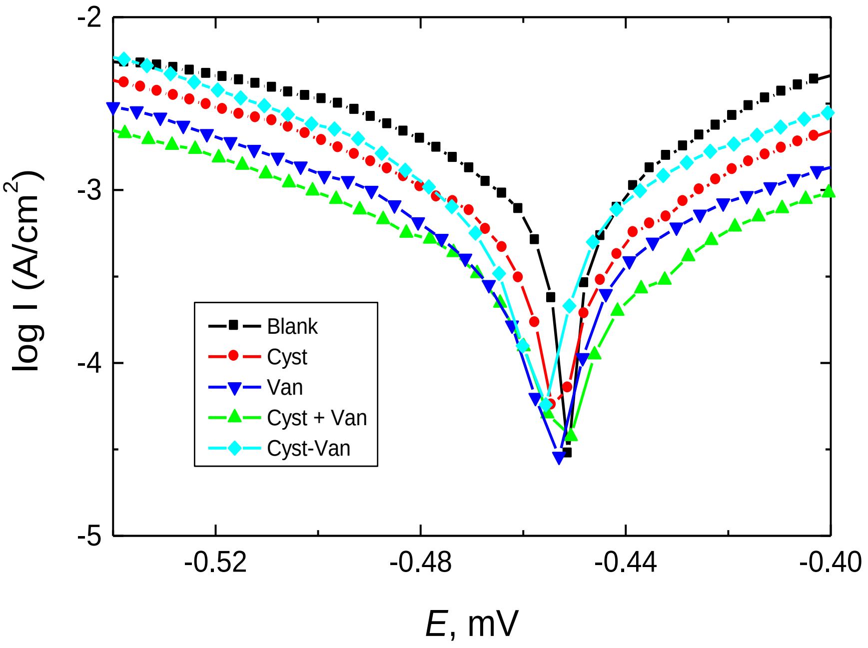


Figure 4. Potentiodynamic polarization curves for mild steel in 0.5 M H_2SO_4 solution in presence of cysteine, vanillin and their mixture (Cyst + Van) and Schiff base formed from cysteine and vanillin (Cyst-Van). Vanillin and Cysteine are $1.0x10^{-4}$ M each.

Vanillin is of larger inhibition efficiency, compared with cysteine, for the corrosion of mild steel in 0.5 M H_2SO_4 solution. The inhibition efficiency in the presence of vanillin and cysteine mixture (73 %) is larger than the summation (52 %) of inhibition efficiencies in their individual presences, i.e., in presence of vanillin (41 %) or cysteine (11 %), pointing to a real synergism between the inhibition exerted by both inhibitors. Synergism means the enhancing of the inhibition efficiency exerted by an inhibitor by another one such that the inhibition efficiency exerted by the two species is larger than the summation of that exerted in their individual presence. The synergism parameter is given by Eq. 2 [70];

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

Table 3. Polarization data for mild steel in 0.5 M H_2SO_4 solution in the absence and presence of cysteine, vanillin, their mixture, with concentrations of 1.0 x 10^{-4} M each, and Schiff base (cyst-van), of same concentration, synthesized from cysteine and vanillin at 25 ^{o}C.

Medium	E_{corr} (mV)	β_c (mV/dec)	β_a (mV/dec)	I_{corr} (µA/cm^2)	θ	% *P*
Blank	-455	110	51	630	--	--
Cysteine	-455	107	64	520	0.17	17
Vanillin	-458	97	62	370	0.41	41
Mixture	-452	94	84	199	0.73	73
Cyst-Van Schiff base	-459	83	93	562	0.13	13

where $\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1\theta_2)$; θ_1 and θ_2 are the degrees of 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. While a synergistic or antagonistic effect is exerted is guided by S_θ values; values larger than one pointes to a real synergism and values smaller than one points to antagonism. The extent of synergism or antagonism based on how far values larger or smaller than unity. In the present case, in the coexisting of vanillin and cysteine S_θ is found to be (1.53) higher than unity, suggesting a real synergistic action.

In contrary, the inhibition efficiency in the presence of Schiff base synthesized from vanillin and cysteine is smaller than the inhibition efficiency exerted by any of them in their separate use referring to antagonism by the Schiff base synthesized from vanillin and cysteine. Calculating the synergism parameter in this case using the above equation was found to equal (0.56) referring to antagonistic effect.

From the above discussion one can tentatively suggest that the aldhydic group of vanillin and the amino group in cysteine play a crucial role in imparting the large inhibition efficiency when present together. When these two groups are involved in the formation of Schiff base and become not freely any more, the inhibition efficiency significantly decreases. The present work give a tentative diagnostic parameter for probing the active site of the studied amino acids and vanillin.

3.2. Adsorption isotherm

Most organic inhibitors exert their inhibition action by the adsorption which depends on several factors including for example chemical structure of inhibitors, and the type of the electrolyte solution

[71]. To examine the adsorption mode of for example one amino acid, e.g., methyl cysteine, in the presence of vanillin, on the surface of the mild steel, the polarization curves in the presence of constant concentration of vanillin and various concentration of methylcysteine were obtained and given in Fig. 5. Data extracted from this figure are shown in Table 4. Inhibition efficiency dependence on the methyl cysteine concentration is given in Fig. 6. Experimental data were fitted with several adsorption isotherms, including Langmuir, Temkin, and Frumkin.

Table 4. Polarization data for mild steel in 0.5 M H_2SO_4 in the absence and presence of constant concentration of vanillin and various concentrations of methylcysteine at 25 ^oC. Data were extracted from Fig. 4.

[m-cyst], **M**	E_{corr} **(mV)**	β_c **(mV/dec)**	β_a **(mV/dec)**	I_{corr} **(µA/cm^2)**	θ	**% *P***
Blank	-458	112	50	612	--	--
1x10^{-6}	-458	89	71	471	0.23	23
5x10^{-6}	-462	87	72	338	0.45	45
1x10^{-5}	-461	84	76	261	0.57	57
5x10^{-4}	-469	80	79	156	0.75	72

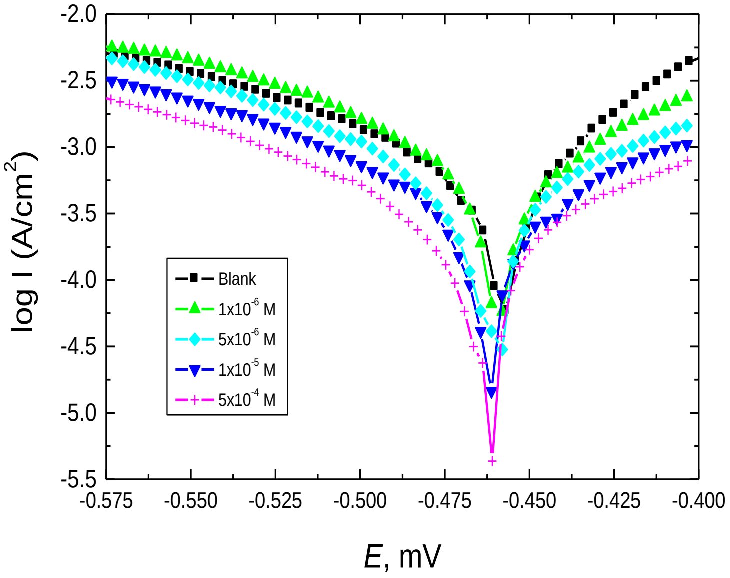


Figure 5. Potentiodynamic polarization curves for mild steel in 0.5 M H_2SO_4 containing 5x10^{-4} M vanillin and different concentrations of methyl-cysteine at 25 ^oC.

Temkin adsorption isotherm (expressed by Eq. 3) was found to fit well with the experimental data as revealed from the correlation coefficients and slopes (Fig. 7) [72]:

$$\exp(-2a\theta) = KC \qquad (3)$$

where, *C* is the concentration of the inhibitor, *a* the molecular interaction parameter and *K* is the equilibrium constant for the adsorption process, which reflects the extent of interaction between the inhibitor and the metal surface. The parameters derived from Temkin, i.e. *K* and change in free energy of adsorption ΔG^{o}_{ads} are found to equal 1.1 x 10^{7} mol^{-1} and - 44.41 kJ mol^{-1}, respectively. The large value of K reflects the stronger ability of adsorption of the inhibitor on the metal surface. ΔG^{o}_{ads} was calculated using Eq. 4 [73];

$$\Delta G^{o}_{ads} = - RT \ln(55.5K_{ads}) \qquad (4)$$

where, R is the molar gas constant (8.314 J K^{-1}), T is temperature in Kelvin and value 55.5 is the concentration of water in mol dm^{3} in solution. The large negative value of ΔG^{o}_{ads} indicates the strong adsorption of the inhibitor. The value of ΔG^{o}_{ads} (*ca*. 44 kJ mol^{-1}) refer to chemisorption mode, i.e., charge sharing or transfer from the inhibitor molecules to the metal surface to form a coordinate type bond. ΔG^{o}_{ads} could be considered as a diagnosis of the mode of adsorption, the values of $\Delta G^{o}_{ads} \geq -40$ kJ mol^{-1} refer that the chemisorption is the most probable mode [73].

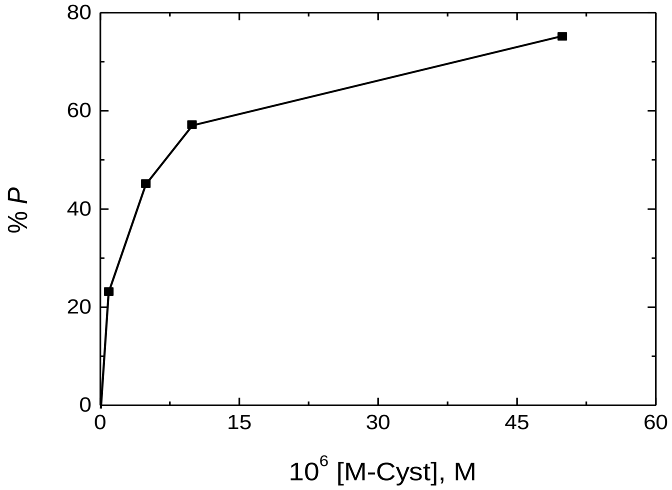


Figure 6. Dependence of inhibition efficiency on methyl-cysteine concentration.

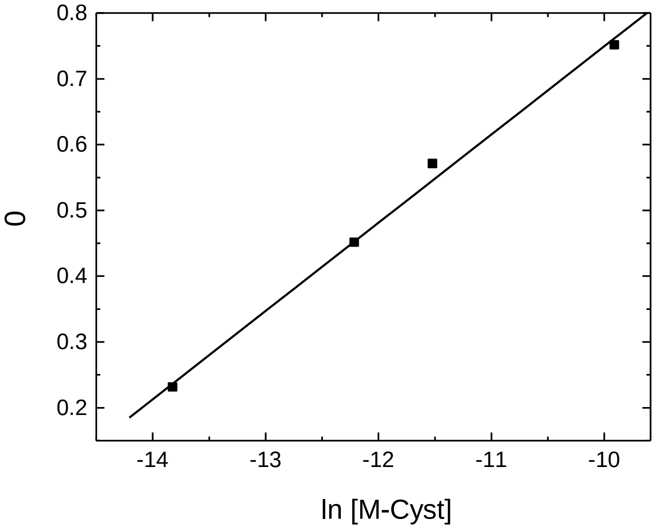


Figure 7. Temkin adsorption isotherms for methyl-cysteine on mild steel in 0.5 M H_2SO_4 at 25 °C.

3.3. SEM measurements

Figure 8 shows SEM images for mild steel samples immersed, for 2 hours, in 0.5 M H_2SO_4

solution in the (a) absence and (b) presence of cysteine and vanillin, $1.0x10^{-4}$ M each. As shown samples immersed in H_2SO_4 containing inhibitor (image b) is less susceptible to corrosion compared with the one immersed in H_2SO_4 solution (image a), revealing the inhibition of corrosion of steel by cysteine-vanillin mixture.

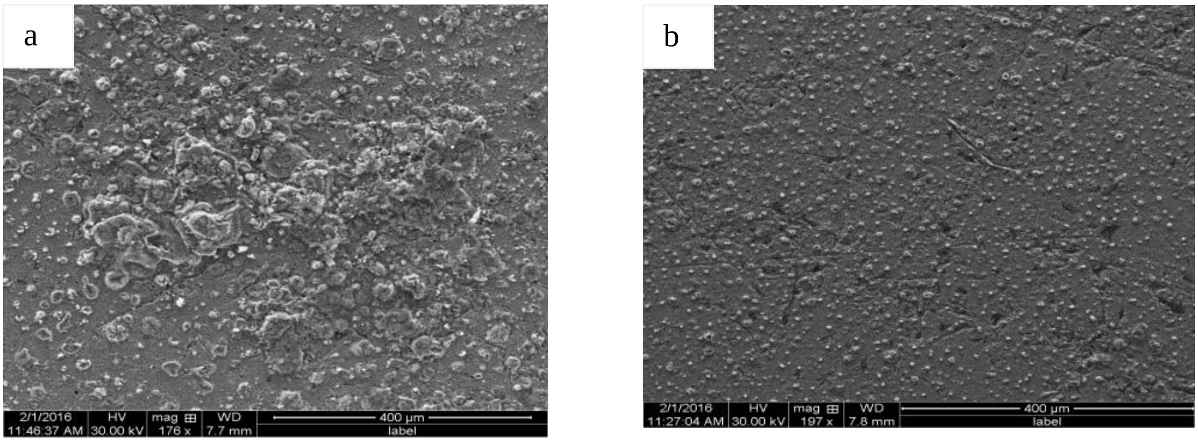


Figure 8. SEM images obtained at mild steel after being immersed in 0.5 M H_2SO_4 solution for 2 hours both in the (a) absence and (b) presence of cysteine-vanillin mixture, $1.0x10^{-4}$ M each.

4. CONSLUSIONS

The inhibition of corrosion of mild steel in sulfuric acid solution by vanillin and several amino acids has been studied, and it has been found that the highest inhibition efficiency is obtained in the presence of vanillin and cysteine mixture. The inhibition efficiency of 87 % is obtained in the presence of vanillin and cysteine, 0.5 mM each. A significant synergism (synergism parameter = 1.53) between vanillin and cysteine for the corrosion inhibition is exerted. Comparing the corrosion inhibition efficiencies of vanillin and cysteine mixture with the Schiff base synthesized from those compounds probed tentatively the active sites of adsorption of the two species.

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