

Novel Corrosion Inhibiting Formulations Involving Amino Acids and Surfactants for Mild Steel in Acid Medium

Mosarrat Parveen and Mohammad Mobin

Corrosion Research Laboratory, Department of Applied Chemistry, Faculty of Engineering and Technology, Aligarh Muslim University, Aligarh, 202 002 (India), e-mail:mosarrat7parveen@gmail.com

Abstract

The researches on replacement of hazardous classical corrosion inhibitors by non toxic inhibitors have gained considerable attention during the last few years. This paper presents the results of studies carried out on inhibiting formulations consisting of amino acids and surfactants for mild steel corrosion in 0.1 M H_2SO_4 in the temperature range of 30-60 °C. The aim of the surfactants addition was to improve the inhibition efficiency of environment friendly but less effective amino acids as inhibitor for mild steel corrosion in acidic medium. The concentration of surfactants was fixed taking into account that environmental safety of inhibitive formulation is least compromised. The techniques used are weight loss measurements, potentiodynamic polarization measurements, scanning electron microscopy (SEM) and atomic force microscopy (AFM). Inhibition efficiency of selected amino acids is synergistically improved in presence of surfactants. Synergism between N-containing amino acid and surfactants is more pronounced than S-containing amino acids and surfactants.

Keywords: Corrosion inhibition, mild steel, synergism, amino acids, surfactants, potentiodynamic polarization measurements, atomic force microscopy, scanning electron microscopy

1. Introduction

The efforts to develop more efficient, economically viable and environmentally compliant methods to prevent corrosion have been ongoing throughout this century. The use of inhibitors is one of the most effective, practical and economic methods to protect metallic surfaces against corrosion in aggressive acid media [1]. Most of the efficient pickling inhibitors are organic compounds containing hetero atoms such as sulfur, nitrogen, oxygen, phosphorus, and multiple bonds or aromatic rings in their structures [2]. The number of lone pairs of electrons and loosely bound π - electrons in these functional groups are the key structural features that determine the inhibitive action of these compounds [3, 4]. These compounds prevent corrosion by blocking the active corrosion sites either by getting adsorbed, or by forming a protective layer or an insoluble complex on the metal surface. However, most of the organic compounds used as corrosion inhibitors are toxic and hazardous to both human beings and the environment [5] and needs to be replaced by nontoxic, environment friendly compounds. As a result, the current research trends is towards the development of nontoxic, economical and more environmentally safe green chemicals as corrosion inhibitors [6-10].

In recent years, there is a considerable amount of effort devoted to develop biodegradable and efficient green corrosion inhibitors extracted from natural plants. Plant

extracts, in addition to being environmentally friendly and ecologically acceptable, are inexpensive, readily available and renewable [11-14]. The inhibition performance of plant extract is normally ascribed to the presence of complex organic species including tannins, alkaloids and nitrogen bases, carbohydrates and proteins as well as hydrolysis products in their composition. The use of polymers as green corrosion inhibitors have drawn considerable attention recently due to their inherent stability and cost effectiveness. Owing to the multiple adsorption sites, polymeric compounds adsorb more strongly on the metal surface compared with their monomer analogues [15-17]. It has been shown by a number of investigators that some amino acids can also act as corrosion inhibitors, which has generated an increasing interest in these compounds [18-27]. Amino acids are attractive as corrosion inhibitors because they are relatively easy to produce with high purities greater than 99% at low cost and are nontoxic, biodegradable and completely soluble in aqueous media. Among the amino acids sulfur containing amino acids has been found to be more efficient corrosion inhibitor [28-30].

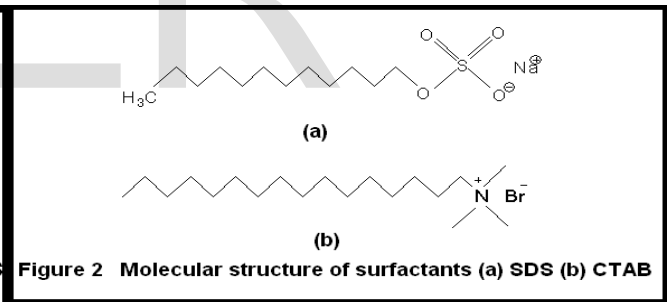
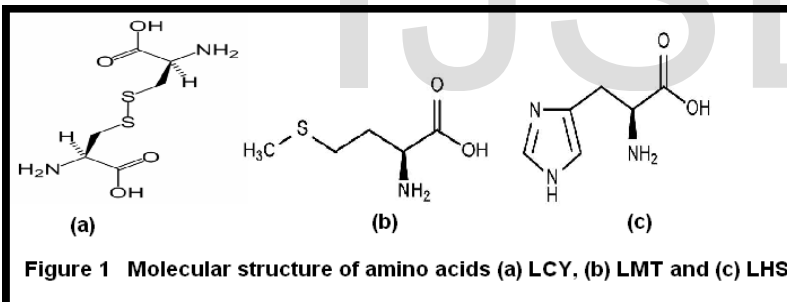
The promising potential application of surfactants as corrosion inhibitors in acidic media has been widely studied during the recent past [31-38]. The corrosion inhibition by surfactant molecules is related to their remarkable ability to influence the properties of surfaces and interfaces. Surfactant inhibitors have many advantages over traditional corrosion inhibitors. For example, they are

easily produced, are economical and possess high inhibition efficiency and low toxicity.

Synergism is one of the most important effects in inhibition process and serves as basis for modern corrosion inhibiting formulations. Synergism of corrosion inhibitors is either due to interaction between constituents of the inhibitor or due to interaction between the inhibitor and one of the ions present in aqueous solution [39]. In most cases, the mechanism of synergism differs from the mechanism of the individual inhibitors. It is, therefore, necessary for corrosion researchers to discover, explore and use synergism in the complicated corrosive media. By taking advantage of synergism the amount of inhibitor applied can be decreased or an environmental friendly but less effective corrosion inhibitor can be used more effectively. The addition of halide ions to organic compounds has shown synergistic effect and resulted in improved inhibition efficiency of many organic compounds [40-42]. However, there remains relatively few works directed towards the synergistic between the different amino acids and other compounds [24, 43-45].

Though the synergistic influence of halide ions on different organic compounds has been adequately investigated there remains relatively few works directed

towards the synergistic between the different organic compounds and surfactants [46]. In a very recent paper the inhibition behavior of methionine combined with cetrimonium bromide (CTAB) and cetylpyridinium bromide (CPB) for Cu corrosion in 0.5 M HCl solution has been reported. It has been shown that combination of methionine with CTAB or CPB provides strong synergistic inhibition effect [47]. A systematic and detailed study on the effect of surfactants on the corrosion inhibition behavior of different environment friendly compounds on the mild steel in acid solutions has been in progress in the authors' lab at Aligarh Muslim University, Aligarh, India. The results have appeared in a number of publications in international journals [48-54]. This paper deals with the standard corrosion studies carried out on inhibiting formulations consisting of three different amino acids namely, L-cystine (LCY) L-methionine (LMT) and L-histidine (LHS) and surfactants sodium dodecyl sulfate (SDS) and cetyltrimethyl ammonium bromide (CTAB) for mild steel corrosion in 0.1 M H₂SO₄. The results of the studies shall provide a better insight into the adsorption and corrosion inhibition mechanism of inhibiting formulations consisting of amino acids and surfactants. The molecular structure of amino acids and surfactants is given in Figure 1 and 2.



2. Results and Discussion

2.1 Weight loss measurements

Weight loss experiments were performed on rectangular mild steel specimens (weight % composition: 0.20% C, 0.53% Mn, 0.036 %Si, 0.011% S, 0.098% P, and balance Fe and size 2.5 × 2.0 × 0.03cm) for duration of 6 h, as per ASTM designation G1-90. The concentration of amino acids was varied from 10 to 500 ppm. Taking into account that environmental safety of inhibitive formulation is least affected the concentration of SDS and CTAB was fixed at 5 and 1 ppm, respectively. The experimental methodology is described elsewhere [48, 49]. The specimens were immersed in triplicate and the average corrosion rate was calculated. The uncertainty or RSD for three replicate

measurements were less than 5%. The % IE data for different amino acids are shown Table 1.

Considering the % IE data, the selected amino acids showed appreciable IE for mild steel corrosion in 0.1 M H₂SO₄ by inhibiting the corrosion reaction by adsorption onto the mild steel surface. In general, the IE increases with increasing amino acid concentration showing a maximum increase in IE at around 200 ppm at 30°C. Further increase in amino acid concentration does not significantly affect the corrosion rate. The IE decreases with increase in temperature. The increased IE with increasing inhibitor concentrations indicates that more amino acid molecules are adsorbed on the steel surface at higher concentration, leading to greater surface coverage and hence formation of a protective film. A relatively low IE at lower concentration

of amino acids could be attributed to the modest surface coverage owing to their smaller molecular area and solubility of adsorbed intermediates formed on the surface. Also a decrease in IE is observed with increase in temperature at all the concentrations studied. This suggests

physical adsorption as the weak Vander Waal's forces responsible for such type of interaction tends to disappear at elevated temperatures. Comparing the IE of three amino acids the S- containing amino acids LCY and LMT appears to perform better than N-containing amino acid LHS.

Table 1 %IE data for mild steel corrosion in 0.1M H₂SO₄ in the presence of varying concentration of LCY, LMT and LHS at 30-60 °C from weight loss measurement

Conc. (ppm)	Inhibition efficiency (%IE)											
	LCY				LMT				LHS			
	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C
10	58.63	50.96	47.31	44.98	53.28	46.34	37.39	20.29	54.61	42.05	40.86	19.32
50	61.89	54.62	52.79	47.59	60.46	53.61	58.50	38.73	58.16	50.66	44.86	19.62
100	74.59	58.55	53.31	50.44	70.21	56.75	51.17	44.22	62.77	58.83	54.39	24.94
200	78.42	66.51	57.79	50.91	75.79	63.61	62.11	45.49	67.11	59.19	54.57	28.93
300	75.08	66.33	58.37	52.66	75.35	68.76	62.44	48.80	67.19	59.36	54.75	28.99
500	74.76	63.22	58.03	51.52	74.02	67.87	62.11	48.54	68.88	65.02	54.39	36.34

The inhibition of mild steel corrosion by amino acids can be explained in terms of their adsorption on the steel surface. In acid solutions, besides their molecular form amino acids can also exist as protonated species, which is caused by the attachment of a proton to the N atom of the NH₂ group. Both molecular and protonated species can adsorb on the corroding steel surface. Considering the adsorption of amino acids on steel surface via molecular form, it may be deduced that the molecules self aggregate at the steel surface arranging into an array of well-ordered stripes of uniform width and separation, depending upon the concentration. The molecules have a long range interaction among them and thus able to cover the surface effectively and results into lowering of the corrosion rate. Since the self-assembly of molecules does not lead to chemical bonding among them, the optimization of the adsorption geometry is only governed by the non-bonding forces e.g. Vander Waals repulsive forces at close range, Lennard-Jones long-range attractive interactions, electrostatic coulomb forces and hydrogen bonding forces. The amino acid molecules lie flat on the steel surface. The energetically most favorable situations are attained when the amino and carboxyl groups as well as the S in the side chain are close to the steel surface. One of the inertial axes of the molecule is nearly parallel with the surface. After the adsorption of the first molecule, the next molecule is preferably arranged in dimer rows with the carboxyl and amino groups facing each other. The bonding of the molecules is accomplished through hydrogen bonds between the amino group and the carboxyl group. These bonds enable the formation of stable dimer rows. Thus it is inferred that the whole of the steel surface is covered by dimer molecules where the two molecules are facing each other. This configuration for molecules in anti-parallel

arrangement is responsible for the high values of IE. Considering the adsorption of amino acids via protonated amino function, the protonated species could interact with the corroding steel surface and may be adsorbed at the cathodic sites and hinder the hydrogen evolution reaction. However, adsorption by positively charged protonated amino function is unlikely to occur as the steel surface is positively charged in acid solutions. In that case the adsorption by protonated amino function on positively charged steel surface may occur through a charged intermediate i.e., SO₄²⁻ anion adsorbed on the steel surface. S-containing amino acids could also interact in molecular form via the S atoms in aliphatic chain, which may be adsorbed at anodic sites and retard Fe electrochemical dissolution. This probably explains higher inhibition efficiency for S-containing amino acids LCY and LMT. In acid medium amino acids are expected to involve both physical and chemical adsorption. However, the variation in the values of %IE with temperature in presence of amino acids compared to blank suggested dominant role of physisorption in the adsorption process. In S-containing amino acids the effectiveness of the adsorption of LMT is slightly inferior to LCY probably due to the presence of S-CH₃ which decreases the stability of the positive charge. The effectiveness of the adsorption of N-containing amino acid LHS may be attributed to the presence of two N (one in imidazole ring and other in the amino group) and O atom (carbonyl group) in the molecule. Further, amino group is easily protonated in the acidic medium, so it could be electrostatically attracted to the cathodic sites on steel surface. The O atom carrying two lone pair of electrons could be adsorbed on the anodic site of steel surface. Therefore, LHS is also expected to involve two ways of adsorption.

To observe the effect of SDS and CTAB on the corrosion inhibition behavior of amino acids, the corrosion of mild steel in 0.1M H₂SO₄ in absence and presence of different concentration of amino acids, in combination with 5 ppm of SDS and 1 ppm of CTAB was separately studied in the temperature range of 30-60°C. The results are produced in Table 2.

The SDS and CTAB also exhibit corrosion inhibition of mild steel in 0.1M H₂SO₄. Considering the adsorption of surfactants molecules at the surfaces, they also has tendency to get adsorbed on steel surface either as individual molecules or as aggregates of various types, depending upon their nature and concentration and exhibit corrosion inhibition of mild steel in 0.1M H₂SO₄. Adsorption of ionic surfactants on a like-charged surface is less understood, but can occur via hydrogen bonding or attractive dispersion forces as is the case for nonionic

surfactants. At low surfactant concentrations, the adsorption behavior can usually be described by the simple electrical double-layer model. Here ionic surfactant monomers adsorb as individual ions without mutual interaction. At higher concentrations tail-tail interactions may begin to cause association of the adsorbed surfactants into aggregates, with the head groups facing the surface. Bilayer at surface is formed, with surfactant monomer head groups in the first layer facing the surface while those of the second layer face the bulk solution. The surfactant molecule adsorption to the steel surface decreases the availability of electrons for undergoing corrosion reaction and thereby decreases the corrosion rate. The micelles like aggregates are formed spontaneously at concentrations well below the bulk cmc and that a complete bilayer is formed at the maximum adsorption of ionic surfactants adsorbing onto surfaces of opposite charge.

Table 2 %IE data for mild steel corrosion in 0.1M H₂SO₄ in the presence of varying concentration of amino acids and surfactants at 30-60 °C from weight loss measurement

Conc. Amino acids +Surfactants (ppm)	Inhibition efficiency (%IE)											
	LCY				LMT				LHS			
	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C
00+SDS 5	27.19	18.66	12.29	5.66	27.19	18.66	12.29	5.66	27.19	18.66	12.29	5.66
10+SDS 5	67.75	58.00	50.10	49.49	66.84	63.41	43.98	21.41	73.76	57.64	41.76	19.76
50+SDS 5	73.62	61.94	55.32	51.77	77.84	66.04	49.05	40.70	76.51	58.39	45.40	20.16
100+SDS 5	77.69	64.59	58.06	53.27	81.29	69.61	52.31	45.67	77.30	63.25	63.95	34.99
200+SDS 5	82.74	70.08	61.75	53.94	82.62	72.14	65.81	47.71	83.33	70.85	65.24	35.25
500+SDS 5	82.25	69.99	58.63	53.67	82.09	74.11	65.59	49.81	86.70	75.44	66.01	40.56
00+CTAB 1	55.86	36.96	17.15	9.61	55.86	36.96	17.15	9.61	55.86	36.96	17.15	9.61
10+ CTAB 1	72.15	64.13	50.62	50.44	73.58	68.67	44.09	26.48	85.82	65.46	50.31	20.09
50+ CTAB 1	75.89	66.79	59.04	54.48	78.19	71.81	53.13	44.38	86.88	65.90	50.52	22.25
100+CTAB 1	78.99	67.34	59.14	55.76	82.62	72.79	56.12	45.69	87.14	74.73	65.08	33.21
200+CTAB 1	84.20	71.45	62.39	56.27	84.22	75.61	66.74	48.49	87.23	76.77	7.41	40.29
500+CTAB 1	82.74	71.36	61.62	56.68	83.69	75.66	65.16	53.59	88.29	77.03	67.92	46.68

The corrosion rate of mild steel in presence of amino acids in combination with surfactants is further reduced in comparison to amino acids alone. The effect of SDS and CTAB is more pronounced on N-containing amino acid LHS. It is observed that the mixture of amino acids and SDS or amino acids and CTAB, increases the IE more than either amino acids or surfactants alone indicating a synergistic effect between amino acids and surfactants. The values of synergism parameter for the various concentration of amino acids studied were calculated from the gravimetric data at 30-60 °C. The values are all greater than unity. This is an indication that the enhanced IE resulting from the addition of surfactants to amino acids is synergistic in nature and proved that addition of a very

small concentration of surfactants can significantly improve the adsorption of amino acids on the mild steel surface. The mixed amino acids and CTAB appears to be more effective as an inhibitor for steel corrosion in 0.1M H₂SO₄ than that the mixture of amino acids and SDS. Considering the effect of surfactants on the corrosion inhibition behavior of different amino acids, the surfactant molecules interact with amino acid molecules, help and direct them to adsorb to the steel surface more firmly. The possible interactions between the SDS and LCY and LMT are: DS⁻ head group- positively charged amino-NH₃⁺; hydrophobic hydrocarbon chain of SDS-side chain (S-containing) of LCY and LMT. Similarly the possible interactions between the CTAB and LCY and LMT are: CTA⁺ head group- -COO⁻ of LCY and

LMT and hydrophobic hydrocarbon chain of CTAB-side chain (S-containing) of LCY and LMT. The forces of interactions which are responsible for the adherence of LHS to the steel surface are; imidazole ring-hydrocarbon chain (of both the SDS and CTAB), positively charged amino -NH₃⁺-DS⁻ headgroup and -COO⁻ (of LHS) -CTA⁺ (headgroup of CTAB). Additionally, the surfactant molecules also adhere to the steel surface unoccupied by the amino acid molecules. The effect of surfactants on the IE of amino acids in 0.1M H₂SO₄ appears to be synergistic in nature. The synergism is more pronounced in case of LHS probably due to higher degree of interaction between LHS and surfactants leading to greater surface coverage by the inhibiting formulation.

2.2 Potentiodynamic polarization measurements

The potentiodynamic polarization measurements were carried out using three electrode assembly, Ag/AgCl

electrode (saturated KCl) as reference electrode, Pt wire as counter electrode and mild steel specimens as working electrode at a scan rate of 0.5mV/s commencing at a potential above 250 mV more active than the stable open circuit potential. The studies were carried out on circular samples of diameter 1cm². All the measurements were carried out at room temperature (30 ± 1°C). Before starting the measurements, the specimen was left in the solution for 30 minutes to attain a steady state which was indicated by a constant potential. The values of electrochemical parameters as deduced from Potentiodynamic polarization curves for the corrosion of mild steel in 0.1M H₂SO₄ in absence and presence of amino acids, SDS, CTAB and amino acids in combination with SDS and CTAB e.g., corrosion potential (*E_{corr}*), corrosion current density (*i_{corr}*) and % IE are shown in Table 3. The %IE was calculated from the measured *I_{corr}* values.

Table 3 Values of electrochemical parameters as obtained from Potentiodynamic polarization curve

Additives	Conc. (ppm)	<i>E_{corr}</i> (mv)	<i>I_{corr}</i> (μA)	(%IE)
Blank	Blank	-507	3.398×10 ⁻⁴	----
SDS	5	-490	2.455×10 ⁻⁴	27.75
LCY	200	-459	5.519×10 ⁻⁵	83.80
LMT	200	-499	7.891×10 ⁻⁵	76.77
LHS	200	-471	8.483×10 ⁻⁵	75.03
LCY+SDS	200+5	-478	4.670×10 ⁻⁵	85.70
LCY+CTAB	200+1	-482	4.860×10 ⁻⁵	86.30
LMT+SDS	200+5	-467	6.766×10 ⁻⁵	80.09
LMT+CTAB	200+1	-498	4.484×10 ⁻⁵	86.81
LHS+SDS	200+5	-469	4.080×10 ⁻⁵	87.99
LHS+CTAB	200+1	-459	3.331×10 ⁻⁵	90.79

The value of *i_{corr}* decreases in presence amino acids which is further decreased in presence of amino acids- surfactant mixture. The values of *E_{corr}* in presence of amino acids and amino acids-surfactant mixture shift to more positive values compared to the blank. The positive shift in *E_{corr}* is more pronounced in presence of amino acids-surfactant mixture, suggesting the dominant role of anodic suppression in the process. The displacement in *E_{corr}* is less than 85mv/SCE suggesting that selected amino acids act a mixed type inhibitors. The results as obtained by electrochemical studies are consistent with the results of the weight loss measurements.

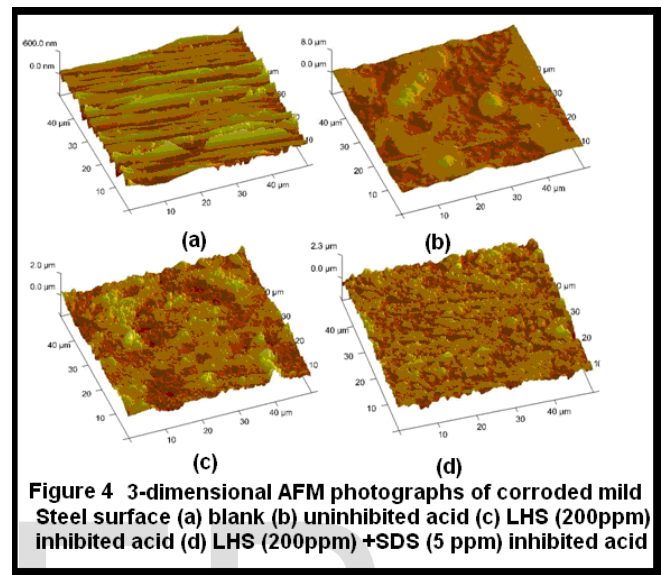
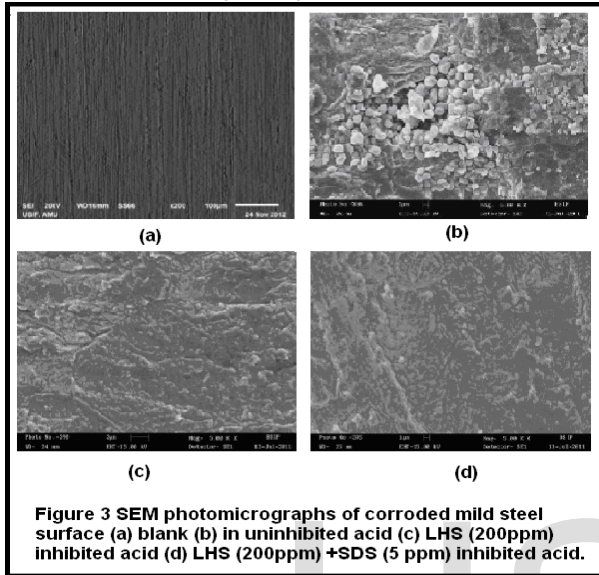
2.3 Surface morphological studies

Surface photographs of the mild steel specimens were obtained by means of SEM and AFM. The typical SEM photographs are shown in Figure 3. Considering the results of the SEM studies on steel prior to its immersion in the

solutions, except the presence of polishing scratches the surface shows the absence of noticeable defects such as pits and cracks. In presence of uninhibited 0.1M H₂SO₄ solutions a damaged and heterogeneous surface is observed. The surface heterogeneity is considerably decreased in the presence of amino acids, which is further reduced in presence of amino acids-surfactant additive. The surface morphologies in presence of amino acids-surfactants are clearly different than those in presence of amino acids alone. SEM results are further proved by surface roughness parameters obtained by AFM photographs taken in uninhibited and inhibited acid solutions at room temperature. In general, in uninhibited acid solution a rough surface is obtained due to rapid corrosion of steel specimen. In presence of amino acids the steel surface is less corroded and a comparatively smoother surface is observed. A smoother layer is as a result of the formation of a protective layer by the adsorbed amino

acids. In presence of amino acids-surfactants inhibited acid solution the surface smoothness is further improved due to the formation of a more compact and continuous adsorbed layer of the inhibitive formulation. Considering the AFM results of LHS (Figure 4); the average surface roughness of mild steel specimen before subjecting to corrosion inhibition studies in 69.9 nm. In presence of uninhibited acid solution, the average roughness of mild steel surface is

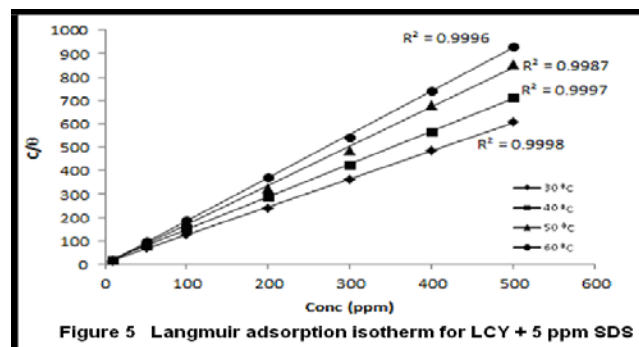
increased to 399 nm. In presence of LCY inhibited acid solution the surface roughness is considerably reduced to 189 nm which is further reduced to 107 nm in presence of LCY+SDS. The AFM results further proved the results as obtained by SEM and confirmed that corrosion inhibition is due to the formation of a protective film by the adsorption of inhibitors.



2.4 Adsorption isotherms

The degree of surface coverage (θ) for various concentrations of amino acids, and amino acids in combination with surfactants have been used to explain the best isotherm to determine the adsorption process. The data were tested graphically by fitting to various isotherms and the best result was obtained for Langmuir adsorption isotherm. The plots of C/θ against, where C is the inhibitor concentration, at 30-60 °C gave a straight line for mild steel in 0.1M H₂SO₄ in the presence of amino acids alone and in

combination with surfactants. The typical Langmuir adsorption isotherm for LCY (200 ppm) in combination with 5 ppm SDS is shown in Figure 5. A linear correlation of slope close to unity for amino acids alone and amino acids in combination with SDS and CTAB suggest that adsorption on mild steel interface in both the cases obeys Langmuir adsorption isotherm at all the temperature studied. This further confirmed that in acid solution the tested surfactants interacted with the amino acids and adsorbed on the mild steel surface as single entity.



2.5 Kinetic/thermodynamic parameters

The apparent activation energy E_a , enthalpy of adsorption, ΔH entropy of adsorption, ΔS and free energy

of adsorption (ΔG_{ads}) for the corrosion of mild steel in 0.1 M H_2SO_4 in the presence of amino acids alone and in combination with surfactants was obtained by following procedures described elsewhere [48]. The values are listed in Table 4.

The E_a values obtained are higher in the presence of amino acids compared to the blank. The E_a values are further increased in presence of surfactants. A change in the value of E_a in presence of additives may be due to the modification of the mechanism of the corrosion process in presence of adsorbed inhibitor molecules. In general, higher values of E_a in presence of additives support physical adsorption mechanism whereas an unchanged or lower value of E_a for inhibited systems compared to the blank is indicative of chemisorption mechanism. The energy barrier

of corrosion process increases with the addition of surfactants indicating that the physisorption create an adsorption film to retard the charge and mass transfer process. The values ΔH increases in presence of additives compared to the free acid solution, this further indicates physical adsorption. In all cases, values of ΔS are positive which indicates a decrease in the system order in presence of additives. The negative values of ΔG_{ads} indicate the stability of the adsorbed additives on the mild steel surface and the spontaneity of the process. The values of ΔG_{ads} obtained in this study are consistent with electrostatic interaction between the charged organic molecules and the charge metals surface which is indicative of physical adsorption.

Table 4 Calculated Values of Kinetic/Thermodynamic Parameters

Additives	Conc. Ppm	E_a (kJmol ⁻¹)	ΔH (kJmol ⁻¹)	ΔS (kJmol ⁻¹ K ⁻¹)	ΔG_{ads} (kJmol ⁻¹)			
					30° C	40°C	50°C	60°C
Blank	----	46.39	43.25	-----	-----	-----	-----	-----
SDS	5	55.31	52.00	20.65	-21.59	-21.15	-20.48	-18.62
CTAB	1	69.37	72.45	80.05	-28.70	-27.54	-24.02	-23.69
LCY	200	65.29	67.53	59.98	-31.03	-30.69	-30.67	-30.85
LMT	200	68.06	68.85	64.17	-17.07	-16.08	-16.43	-15.07
LHS	200	67.95	63.34	10.42	-15.97	-15.61	-15.59	-13.09
LCY+SDS	200+5	71.47	73.22	76.73	-31.93	-31.12	-31.11	-31.19
LCY+CTAB	200+1	72.51	74.35	79.87	-32.19	-31.29	-31.19	-31.45
LHS + SDS	200+5	84.36	78.56	55.49	-18.23	-16.95	-16.79	-13.89
LHS+ CTAB	200+1	89.56	84.49	72.88	-19.02	-17.75	-17.05	-14.48
LMT+SDS	200+5	76.00	76.68	87.13	-18.08	-17.10	-16.88	-15.31
LMT+ CTAB	200+1	78.29	80.59	99.93	-18.36	-17.57	-16.96	-15.41

3. Conclusions

1. Amino acids L-cystine, L-methionine and L-histidine showed good performance as corrosion inhibitor for mild steel in 0.1 M H_2SO_4 . The inhibition efficiency of all the three amino acids is synergistically improved in presence of surfactants SDS and CTAB. The highest inhibition efficiency of the inhibitor formulations was observed at around 200 ppm of amino acids and surfactants at 30°C.
2. S-containing amino acids L-cystine and L-methionine perform better than N-containing amino acid L-histidine. However, the synergism between N-containing amino acid and surfactants is more

4. Reference

[1] M. Behpour, S.M. Ghoreishi, A. Gandomi-Niasar, N. Soltani and M. Salavati-Niasari, *J. Mater. Sci.*, 44 (2009) 2444.

pronounced than S-containing amino acids and surfactants.

3. The adsorption mechanism for amino acids and amino acids-surfactants mixture fit well the Langmuir adsorption isotherm at all the concentrations and temperatures studied.
4. The studied inhibitive formulations act a mixed inhibitor.
5. SEM and AFM studies showed different surface morphologies for corroded steel in amino acids and amino acids-surfactant inhibited acid solutions and further confirmed the higher inhibitive effect of amino acids surfactants mixture than amino acids alone.

[2] A. Ostovari, S.M. Hoseinie, M. Peikari, S.R. Shadizadeh, and S.J. Hashemi, *Corros. Sci.*, 51 (2009) 1935.

- [3] S.K. Shukla, A.K. Singh, I. Ahamad and M.A. Quraishi, *Mater. Lett.*, 63 (2009) 819.
- [4] S.K. Shukla and M.A. Quraishi, *J. Appl. Electrochem.*, 39 (2009) 1517.
- [5] M.M. Solomon, S.A. Umoren, I.I. Udousoro and A.P. Udoh, *Corros. Sci.*, 52 (2010) 1317.
- [6] A.K. Singh and M.A. Quraishi, *Corros. Sci.*, 52 (2010) 152.
- [7] M.S. Morad, *Corros. Sci.*, 50 (2008) 436.
- [8] O.K. Abiola and A.O. James, *Corros. Sci.*, 52 (2010) 661.
- [9] F.S. de Souza and A. Spinelli, *Corros. Sci.*, 51 (2009) 642.
- [10] S.A. Umoren, I.B. Obot and N.O. Obi-Egbedi, *J. Mater. Sci.*, 44 (2009) 274.
- [11] L. Valek and S. Martinez, *Mater. Lett.*, 61 (2007) 148.
- [12] P.B. Raja and M.G. Sethuraman, *Mater. Lett.*, 62 (2008) 113.
- [13] A.M. Abdel-Gaber, B.A. Abd-El-Nabey and M. Saadawy, *Corros. Sci.*, 51 (2009) 1038.
- [14] M.A. Quraishi, A. Singh, V.K. Singh and D.K. Yadav, *Mater. Lett.*, 122 (2010) 114.
- [15] D.P. Schweinsberg, G.A. Hope, A. Trueman and V. Otieno-Alego, *Corros. Sci.*, 38 (1996) 587.
- [16] Y. Abed, Z. Arrar, B. Hammouti, M. Taled, S. Kertit and A. Mansri, *Anti-Corros. Methods Mater.*, 48 (2001) 304.
- [17] R. Rosliza and W.B. Wan Nik, *Curr. Appl. Phys.*, 10 (2009) 221.
- [18] H. Ashassi-Sorkhabi, M.R. Majidi and K. Seyyedi, *Appl. Surf. Sci.*, 225 (2004) 176.
- [19] M. Zerfaoui, H. Oudda, B. Hammouti, S. Kertit and M. Benkaddour, *Prog. Org. Coat.*, 51 (2004) 134.
- [20] D.Q. Zhang, L.X. Gao and G.D. Zhou, *J. Appl. Electrochem.*, 35 (2005) 1081.
- [21] H. Ashassi-Sorkhabi, Z. Ghasemi and D. Seifzadeh, *Appl. Surf. Sci.*, 249 (2005) 408.
- [22] A.B. Silva, S.M.L. Agostinho, O.E. Barcia, G.G.O. Cordeiro and E.D. Elia, *Corros. Sci.*, 48 (2006) 3668.
- [23] E.E. Oguzie, Y. Li, and F.H. Wang, *Electrochim. Acta*, 53 (2007) 909.
- [24] E.E. Oguzie, Y. Li and F.H. Wang, *J. Colloid Interface. Sci.*, 310 (2007) 90.
- [25] D.Q. Zhang, Q.R. Cai, L.X. Gao, and K.Y. Lee, *Corros. Sci.*, 12 (2008) 3615.
- [26] H. Saifi, M.C. Bernard, S. Joiret, K. Rahmouni, H. Takenouti and B. Talhi, *Mater. Chem. Phys.*, 120 (2010) 661.
- [27] J.J. Fu, S.N. Li, L.H. Cao, Y. Wang, L.H. Yan and L.D. Lu, *J. Mater. Sci.*, 45 (2010) 979.
- [28] M.S. Morad, *J. Appl. Electrochem.*, 35 (2005) 889.
- [29] M. Ozcan, F. Karadag and I. Dehri, *Colloids Surf A.*, 316 (2008) 55.
- [30] K.F. Khaled, *J. Solid State Electrochem.*, 13 (2009) 1743.
- [31] M.A. Migahed and A.M. Al-Sabagh, *Chem. Engg. Comm.*, 196 (2009) 1054.
- [32] M.L. Free, *Corrosion*, 58 (2002) 1025.
- [33] M. Saleh and A.A. Atia, *J. Appl. Electrochem.*, 36 (2006) 899.
- [34] W.L. Wang and M.L. Free, *Corros. Sci.*, 46 (2004), 2601.
- [35] A.A. Atia and M.M. Saleh, *J. Appl. Electrochem.*, 33 (2003) 171.
- [36] T.Y. Soror and M.A. El-Ziady, *Mater. Chem. Phys.*, 77 (2002) 697.
- [37] X. Li, L. Tang, H. Lie, G. Mu and G. Lie, *Mater. Lett.*, 62 (2008) 2321.
- [38] M. El Azhar, B. Mernari, M. Traisnel, F. Bentiss and M. Lagrenee, *Corros. Sci.*, 43 (2001) 2227.
- [39] N.O. Eddy and A.O. Odiongenyi, *J. Phys. Chem.*, 3 (2007) 56.
- [40] E.E. Ebenso, *Mater. Chem. Phys.*, 79 (2003) 58.
- [41] D.Q. Zhang, L.X. Gao and G.D. Zhou, *J. Appl. Electrochem.*, 33 (2003) 361.
- [42] L.B. Tang, G.N. Mu and G.H. Liu, *Corros. Sci.*, 45 (2003) 2251.
- [43] K.M. Ismail, *Electrochim. Acta*, 52 (2007) 7811.
- [44] D.Q. Zhang, Q.R. Cai, X.M. He, L.X. Gao, and G.S. Kim, *Mater. Chem. Phys.* 114 (2009) 612.
- [45] D.Q. Zhang, B. Xie, L.X. Gao, Q.R. Cai, H.G. Joo and K.Y. Lee, *Thin Solid Films*, 520 (2011) 350.
- [46] M.Z.A. Rafiquee, N. Saxena, S. Khan, and M.A. Quraishi, *Mater. Chem. Phys.*, 107 (2008) 528.
- [47] D.Q. Zhang, B. Xie, L.X. Gao, H.G. Joo and K.Y. Lee, *J. Appl. Electrochem.*, 41 (2011) 491.
- [48] M. Mobin, M.A. Khan, and M. Parveen, *J. Appl. Polym. Sci.*, 121 (2011) 1558.
- [49] M. Mobin, M. Parveen and M.A. Khan, *Portugaliae Electrochimica Acta*, 29 (6) (2011) 391-403.
- [50] M. Mobin, M. Parveen and M.Z.A. Rafiquee, *J. of Materials Engineering and Performance*, 22(2) (2013) 548-556.
- [51] M. Mobin and M.A. Khan, *Chemical Engg. Communication*, 200 (9) (2013) 1149-1169.
- [52] M. Mobin and M.A. Khan, *J. of Dispersion Science and Tech*, DOI:10.1080/01932691.2012.751031.
- [53] M. Mobin and M. Parveen, *J. of Dispersion Science and Tech*, DOI: 10.1080/01932691.2013.773443.
- [54] M. Mobin, M. Parveen and M.Z.A. Rafiquee, *Arabian Journal of Chemistry*, DOI: 10.1016/j.arabjc.2013.04.006.

1. **Dr. Mosarrat Parveen** is a Guest Faculty at the Department of Applied Chemistry, Faculty of Engineering & Technology, Aligarh Muslim University, Aligarh, India.
2. **Dr. Mohammad Mobin** is Senior Professor at the Department of Applied Chemistry, Faculty of Engineering & Technology, Aligarh Muslim University, Aligarh, India.

IJSER