

Inhibition of Mild Steel Corrosion in Acidic Medium Using Starch and Surfactants Additives

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ABSTRACT: The corrosion inhibition of mild steel in 0.1M H₂SO₄ in presence of starch (polysaccharide) was studied using weight loss and potentiodynamic polarization measurements in the temperature range of 30–60°C. Starch inhibits the corrosion rates of mild steel to a considerable extent; the maximum inhibition efficiency (%IE) being 66.21% at 30°C in presence of starch concentration of 200 ppm. The effect of the addition of very small concentration of sodium dodecyl sulfate and cetyl trimethyl ammonium bromide on the corrosion inhibition behavior of starch was also studied. The IE of starch significantly improved in presence of both the surfactants. The effect of surfactants on the corrosion inhibition behavior of starch

appears to be synergistic in nature. Starch alone and in combination with surfactants is found to obey Langmuir adsorption isotherm from the fit of the experimental data of all concentration and temperature studied. Phenomenon of physical adsorption is proposed from the trend of IE with temperature and also the values E_a , ΔG_{ads} , and Q_{ads} obtained. The results obtained by potentiodynamic polarization measurements are consistent with the results of the weight loss measurement. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 1558–1565, 2011

Key words: corrosion inhibition; mild steel; polysaccharide; surfactant; adsorption isotherm

INTRODUCTION

The corrosion of iron and steel is a subject of fundamental, academic, and industrial concern and has received a considerable amount of attention. The use of corrosion inhibitors is one of the most practical methods for the protection against corrosion, especially in acid media. The corrosion inhibitors are generally used to protect metals against the attack of the acid solutions, which are widely used in acid pickling, industrial cleaning, acid descaling, and oil-well acidizing, etc. The acid pickling of steel in various industries is generally carried out at temperatures up to 60°C. Corrosion inhibitors are added to the solution during pickling to reduce the degree of metal attack and rate of acid consumption.^{1–5} The inhibitors prevent corrosion either by being adsorbed on the surface of metals or by forming a protective layer, or by causing the formation of insoluble complex. Most of the inhibitors used in industry are organic compounds containing multiple bonds in their molecules that mainly contain nitrogen, sulphur, and/or oxygen atoms through which they get adsorbed on the metal surface.^{6–8} However,

most of these substances are toxic and using them is harmful for both human health and environment.

In recent times, a number of polymers have been exploited as corrosion inhibitors due to their inherent stability and cost effectiveness. The functional groups of the polymers form complexes with metal ions, which occupy a large surface area and thus protecting the metals from corrosive agents present in solution.⁹ The polymer inhibitors which have been widely examined include: polyethylene glycol, polyvinyl alcohol, polyvinyl pyridine, polyvinyl pyrrolidone, polyethylenimine, polyacrylic acid, and poly acrylamide.^{10–13} A survey of literature shows that a number of naturally occurring materials such as natural honey,^{14,15} henna,¹⁶ guar gum,¹⁷ opuntia extract,¹⁸ and jojoba oil¹⁹ have shown promising results as corrosion inhibitors for iron and steel in acidic solutions. Recently, inhibition of mild steel corrosion in H₂SO₄ using synthetic (polyethylene glycol) and naturally occurring (gum arabic) polymer was studied in the temperature range of 30–60°C.²⁰ Both the polymers were found to act as inhibitors but synthetic polymer was more effective than natural polymer.

Starch is a natural polymer, available in abundance at low cost, renewable, and biodegradable. Chemically it is a polysaccharide carbohydrate consisting of a large number of glucose units joined together by glycosidic bonds. Starch is produced by all green plants as an energy store. It contains two

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structurally different components namely, amylose (15–20%), and amylopectin (80–85%). The amylose is composed of large linear chain of α (1–4) linked α -D-glucopyranosyl residue, whereas amylopectin is a branching form of α -glycon linked by α (1–6) linkages. The molecular structure of the starch suggests that it has strong potential to become an effective corrosion inhibitor. A survey of literature indicates that only few references are available dealing with the corrosion inhibition effect of starch on aluminum^{21,22} and steel.²³ More recently, modified cassava starches were evaluated as corrosion inhibitor for carbon steel under alkaline conditions in 200 mg/L NaCl solutions.²⁴ The inhibitive properties were studied by means of electrochemical impedance spectroscopy. The starches were found to show corrosion inhibitive properties; their protection level depended on the type and amount of active groups present in the molecules. Surfactants have been used as corrosion inhibitors either alone or in combination with other compounds to improve their performance as inhibitors. The surfactant molecules possess strong adsorption ability to the metallic surfaces. The adsorb molecules form a monolayer or bilayer hemimicelles or admicelles, depending upon the surfactant concentration and prevent the acid to attack the surface, and thus reduce the corrosion attack.^{25–28} The surfactant can be used either alone or in mixtures with other compounds.

The majority of the acidic inhibitors have been known for their specificity of inhibition action. A combination of inhibitors is likely to provide multiple effects required for effective corrosion inhibition. The addition of halide ions to organic compounds has shown synergistic effect and resulted in improved inhibition efficiency (IE) of many organic compounds and reported in the literature.^{29–31} However, the influence of surfactants on the corrosion inhibition behavior of organic compounds is very scanty.³² This work was undertaken to investigate the inhibition of mild steel corrosion in acidic medium using starch for which no reference is available in the literature. Further, the effect of the addition of very small concentration of sodium dodecyl sulfate (SDS) and cetyl trimethyl ammonium bromide (CTAB) on the corrosion inhibition behavior of starch has also been investigated.

EXPERIMENTAL

Material preparation

The mild steel coupons having composition 0.19% C, 0.055% Si, 0.366% Mn, 0.069% P, 0.087% S, 0.074% Ni, 0.075% Cr 0.11% Mo and balance Fe were used for corrosion inhibition studies. The mild steel sheets were mechanically press-cut into coupons of dimen-

sion $2.5 \times 2 \times 0.03$ cm. The coupons were machined and abraded on different grades emery papers, washed with double distilled water, degreased with absolute ethanol and finally dried in acetone. A hole of 1 mm dia was made near the edge of the specimen for hooking. The treated coupons were then stored in moisture-free desiccators before their use in corrosion studies. Starch and surfactants SDS and CTAB (MERCK, India) were used as received. The starch selected for the investigation is soluble extra pure having solubility of 50 g/L (90°C), bulk density 300 kg/cm³ and the pH value 6.0–7.5 (20 g/L H₂O, 25°C). The concentration of starch prepared and used for the study ranges from 1 to 500 ppm. The concentration of H₂SO₄ prepared and used was 0.1M. All solutions were made using double distilled water. The study was carried out at 30–60°C maintaining the temperatures using a thermostated water bath.

Weight loss measurements

The weight loss experiments were performed for duration of 8 h as per ASTM designation G1–90. The cleaned mild steel coupons were suspended in 250-mL beakers containing 200 mL of test solutions maintained at 30–60°C in a thermostated bath with the aid of glass rods and hooks. The concentration of inhibitor (starch) in H₂SO₄ was kept between 1 and 500 ppm. The weight loss taken was the difference between the weight at a given time and the original weight of the coupons. The measurements were carried out for the uninhibited solution (blank) and solutions containing starch and starch-surfactant mixtures. The corrosion rates were determined using the equation:

$$\text{Corrosion rate (mpy)} = \frac{534 W}{\rho A t} \quad (1)$$

where, W is weight loss in mg; ρ is the density of specimen in g/cm³; A is the area of specimen in sq. inch and t is exposure time in hours.

The %IE of starch, surfactants and starch-surfactant mixtures was evaluated using the following equation:

$$(\%IE) = \frac{CR_o - CR_i}{CR_o} \times 100 \quad (2)$$

where, CR_o is the corrosion rate of mild steel in absence of inhibitor and CR_i is corrosion rate of mild steel in presence of inhibitor.

Potentiodynamic polarization measurements

Experiments were performed using a conventional three electrode cell assembly, using an EG&G potentiostat/Galvanostat, model 263A. The experiments were carried out using a corrosion cell from EG&G,

TABLE I
Calculated Values of Corrosion Rate (mpy) and Inhibition Efficiency (%IE) for Mild Steel in 0.1M H₂SO₄ in the Absence and the Presence of Starch at 30–60°C from Weight Loss Measurement

Starch conc. (ppm)	Corrosion rate (mpy)				Inhibition efficiency (%IE)			
	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C
Blank	200.88	522.74	1132.70	2087.66	–	–	–	–
1	90.99	294.71	704.42	1516.99	54.70	43.62	37.81	27.33
5	77.22	227.75	536.51	1144.50	61.56	56.43	52.63	45.18
10	71.28	217.18	521.41	1081.31	64.45	58.45	53.97	48.20
50	69.66	207.64	482.42	1002.36	65.32	60.28	57.41	51.99
100	68.58	209.53	469.97	969.30	65.86	59.92	58.51	53.57
200	67.884	200.49	462.73	948.79	66.21	61.65	59.15	54.55
500	70.74	201.39	461.09	948.79	64.78	61.47	59.29	54.55

model K0047 with Ag/AgCl electrode (saturated KCl) as reference electrode, Pt wire as counter electrode and mild steel coupons as working electrode. The working electrode was polished with 320, 600, 800 grade emery papers, washed with distilled water, and degreased with acetone. Before starting the measurements, the specimen was left into the solution for 30 min to attain the steady state. The experiments were performed with the potential of –250 to 250 mV at a scan rate of 0.166 mV/s. All the experiments were carried out at room temperature (30 ± 1°C). The electrochemical experiments data were collected and analyzed by electrochemical software PowrSuit ver. 2.58. The IE was calculated from the measured I_{CORR} values using the relationship:

$$(\%IE) = \frac{i_{\text{CORR}}^0 - i_{\text{CORR}}}{i_{\text{CORR}}^0} \times 100 \quad (3)$$

where, i_{CORR}^0 is corrosion current density in the absence of inhibitor and i_{CORR} is corrosion current density in the presence of inhibitor.

RESULTS AND DISCUSSION

Weight loss measurements

The corrosion of mild steel in 0.1M H₂SO₄ in the absence and presence of starch as inhibitor was studied using weight loss technique at temperature range of 30–60°C. The calculated value of corrosion rates and IE for the starch at different concentrations and temperatures is shown in Table I. From the table, it is clearly seen that the corrosion rates are reduced in presence of starch as compared to the free acid solution. Also the corrosion rate increased with increase in temperature at all concentrations. The plot of IE as a function of starch concentrations at 30–60°C (Fig. 1) reveals that IE increases with increase in starch concentration showing a maximum efficiency of 66.21% at 30°C temperature in presence of starch concentration of 200 ppm; further addition of starch does not significantly influence

the IE. The inhibition of mild steel corrosion in the presence of starch could be attributed to the adsorption of the compound on to mild steel surface, which blocks the metal and thus do not permit the corrosion process to take place. Starch can be adsorbed by the interaction between the lone pair of electrons of the oxygen atom and the steel surface. The presence of d π vacant orbital of low energy in the iron atom, as observed in transition group metals, facilitates the adsorption process. In acid, medium starch may be partially hydrolyzed into simpler carbohydrates but the products with higher hydrophilicity than starch is likely to go into the bulk water. As the hydrolysis is quite slow, only negligible starch molecules are expected to hydrolyze and desorb from the steel surface. Also, the starch in bulk water may occupy the steel surface as the molecules are in dynamic equilibrium. So, even after slow hydrolysis, inhibition by starch is effective.

The increased IE with increasing starch concentration indicates that more inhibitor molecules are adsorbed on the steel surface leading to the formation of a protective film.³³ A decrease in IE with increasing temperature suggests possible desorption

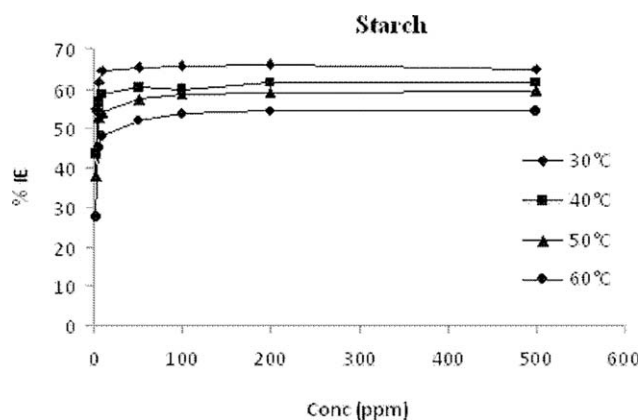


Figure 1 Plot of inhibition efficiency (% IE) against starch concentration for mild steel in 0.1 M H₂SO₄ at different temperatures.

TABLE II
Calculated Values of Corrosion Rate (mpy), Inhibition Efficiency (%IE) and Synergism Parameter (S_1) for Mild Steel in 0.1M H_2SO_4 in the Absence and the Presence of Varying Concentration of Starch with SDS at 30–60°C from Weight Loss Measurement

Starch conc. (ppm)	SDS conc. (ppm)	Corrosion rate (mpy)				Inhibition efficiency (%IE)				Synergism parameter (S_1)			
		30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C
Blank	Blank	200.88	522.74	1132.70	2087.66	–	–	–	–	–	–	–	–
–	5	138.96	383.16	990.67	1939.00	30.82	26.70	12.54	7.12	–	–	–	–
1	5	69.61	254.30	634.62	1352.33	65.35	51.35	43.97	35.22	1.313	1.377	1.125	0.948
5	5	63.93	182.83	456.04	1026.65	68.17	65.02	59.74	50.82	1.360	1.283	1.092	1.029
10	5	61.54	181.21	480.73	986.83	69.36	65.33	57.56	52.73	1.379	1.308	1.158	1.050
50	5	61.40	179.60	417.99	940.75	69.43	65.64	63.09	54.94	1.390	1.330	1.110	1.077
100	5	61.71	177.60	414.73	924.77	69.28	66.02	63.38	55.70	1.401	1.317	1.123	1.091
200	5	62.78	179.75	409.84	903.27	68.75	65.61	63.82	56.73	1.417	1.352	1.125	1.088
500	5	65.46	178.14	421.79	903.27	67.41	65.92	62.76	56.73	1.424	1.343	1.147	1.080

of some of the adsorbed starch molecules from the metal surface at higher temperatures. This behavior shows that the starch was physically adsorbed on the metal surface.³⁴ As the temperature increases, the quantity of equilibrium of adsorption decreases³⁵ and as a result, the plot of higher temperatures is below the lower ones. This is clearly demonstrated in Figure 1, which shows that starch is physically adsorbed on the steel surface since the plots of higher temperatures are under that of lower ones. The decrease in IE with increasing temperature may be due to the fact that most of the effects at elevated temperatures are adverse to corrosion inhibition by increasing the corrosion rate and decreasing the tendency of the starch to be adsorbed on the steel surface.

To observe the effect of SDS and CTAB on the corrosion inhibition behavior of starch, the corrosion of mild steel in 0.1M H_2SO_4 in absence and presence of varying concentration of starch in combination with SDS (5 ppm) and CTAB (1 ppm) was separately studied in the temperature range of 30–60°C by weight loss technique. The results are shown in Tables II and III. It is observed that the corrosion rates of mild steel in 0.1M H_2SO_4 in presence of

starch in combination with surfactants is further reduced in comparison to starch alone. Plots of IE versus concentration of starch in combination with surfactants at 30–60°C are shown in Figures 2 and 3. The anionic SDS binds with starch through electrostatic interaction, thus helps to adsorb at the metal surface more firmly and display higher IE. The IE of starch in presence of 1 ppm of CTAB is also higher than the starch alone. It may be due to the adsorption of starch to the metal surface by binding with CTAB as co-ions or through hydrophobic interaction. The effect of surfactants on the IE of starch in 0.1M H_2SO_4 appears to be synergistic in nature.

Synergism considerations

The synergism parameter, S_1 was evaluated using the relationship.³⁶

$$S_1 = \frac{1 - I_{1+2}}{1 - I'_{1+2}} \quad (4)$$

where, $I_{1+2} = (I_1 + I_2)$; I_1 is IE of starch and I_2 is IE of surfactant, SDS/CTAB and I'_{1+2} is IE of starch in combination with surfactant. S_1 Approaches 1 when

TABLE III
Calculated Values of Corrosion Rate (mpy), Inhibition Efficiency (%IE) and Synergism Parameter (S_1) for Mild Steel in 0.1M H_2SO_4 in the Absence and Presence of Varying Concentration of Starch with CTAB at 30–60°C from Weight Loss Measurement

Starch conc. (ppm)	CTAB conc. (ppm)	Corrosion rate (mpy)				Inhibition efficiency (%IE)				Synergism parameter (S_1)			
		30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C
Blank	Blank	200.88	522.74	1132.70	2087.66	–	–	–	–	–	–	–	–
–	1	134.34	407.38	964.18	1849.42	33.12	22.07	14.88	11.41	–	–	–	–
1	1	59.15	196.32	579.43	1311.80	70.55	62.44	48.84	37.16	1.248	1.053	1.080	1.044
5	1	54.68	181.66	469.55	1053.54	72.78	65.25	58.54	49.53	1.305	1.206	1.156	1.145
10	1	59.67	189.26	448.78	1020.80	70.29	63.79	60.38	51.10	1.394	1.266	1.143	1.170
50	1	62.60	198.24	453.68	974.23	68.84	62.08	59.95	53.33	1.436	1.332	1.209	1.192
100	1	63.91	201.07	459.12	956.83	68.18	61.53	59.47	54.17	1.458	1.338	1.238	1.203
200	1	67.06	198.81	463.10	958.66	66.62	61.97	59.11	54.08	1.498	1.357	1.257	1.224
500	1	68.19	199.94	465.30	960.39	66.05	61.75	58.92	53.99	1.489	1.359	1.263	1.226

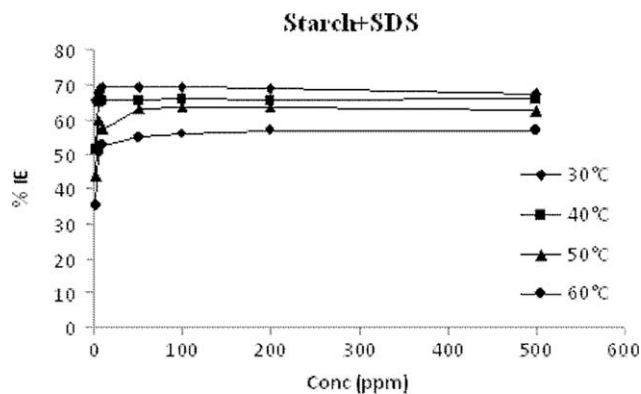


Figure 2 Plot of inhibition efficiency (% IE) against (starch + 5 ppm SDS) concentration for mild steel in 0.1M H_2SO_4 at different temperatures.

no interaction between inhibitor (starch) and the surfactant exist, whereas $S_1 > 1$ indicate a synergistic effect. In the case of $S_1 < 1$, antagonistic behavior prevails which may be attributed to competitive adsorption.

The values of the synergism parameter for the various concentrations of starch studied were calculated from the gravimetric data at 30–60°C, and the results are presented in Tables II and III. The synergism parameter S_1 is found to be greater than unity indicating that the enhanced IE caused by the addition of surfactants is only due to synergism. The addition of a very small amount of surfactant can improve the adsorption of starch on the mild steel.

Adsorption considerations

The adsorption of organic compounds on metal surfaces can be described by two main types of interactions namely, physical adsorption and chemical adsorption. These adsorptions are dependent on the electronic structure of the metal, the nature of the electrolyte and the chemical structure of the or-

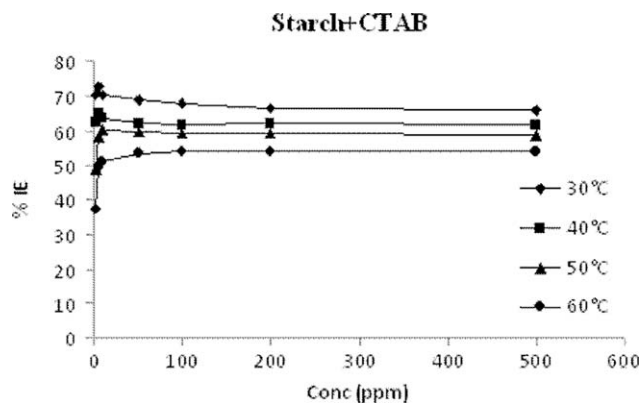


Figure 3 Plot of inhibition efficiency (% IE) against (starch + 1 ppm CTAB) concentration for mild steel in 0.1M H_2SO_4 at different temperatures.

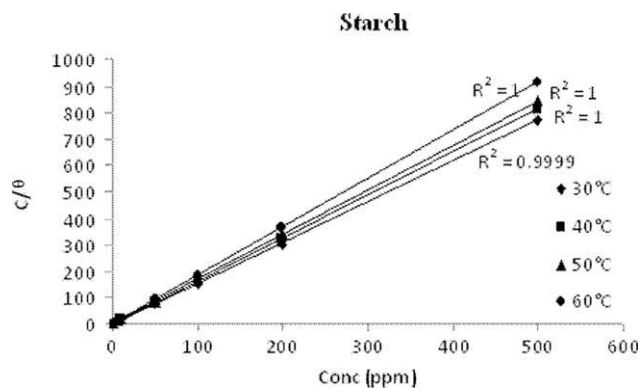


Figure 4 Langmuir adsorption isotherm for starch adsorbed on mild steel surface in 0.1M H_2SO_4 at different temperatures.

ganic compounds. The character of adsorption of starch alone and starch in combination with SDS and CTAB was elucidated from the values of degree of surface coverage (θ) calculated from the weight loss data. Attempts were made to fit the θ values to various adsorption isotherms but best results were obtained for Langmuir adsorption isotherm.

The plots of C/θ against C are drawn which is characteristics of Langmuir adsorption isotherm given by equation:

$$\frac{C}{\theta} = \frac{1}{k} + C \quad (5)$$

where θ is the degree of surface coverage, K is the equilibrium constant of the adsorption process and C is the starch concentration. The plots of C/θ versus C for mild steel corrosion in 0.1M H_2SO_4 for starch alone and starch in combination with SDS and CTAB at temperature 30–60°C is shown in Figures 4–6. A linear correlation of slope close to unity suggests that adsorption of starch alone and starch in combination with SDS and CTAB on mild steel

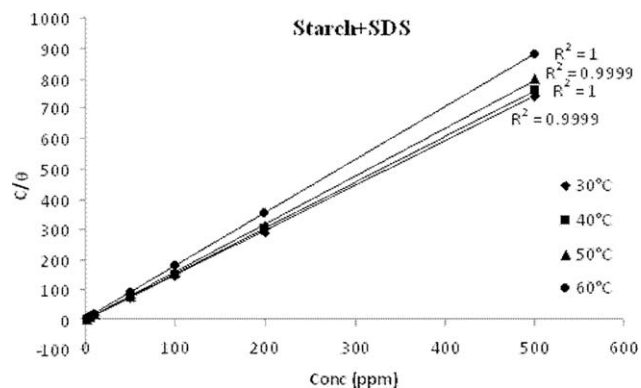


Figure 5 Langmuir adsorption isotherm for (starch + 5 ppm SDS) adsorbed on mild steel surface in 0.1M H_2SO_4 at different temperatures.

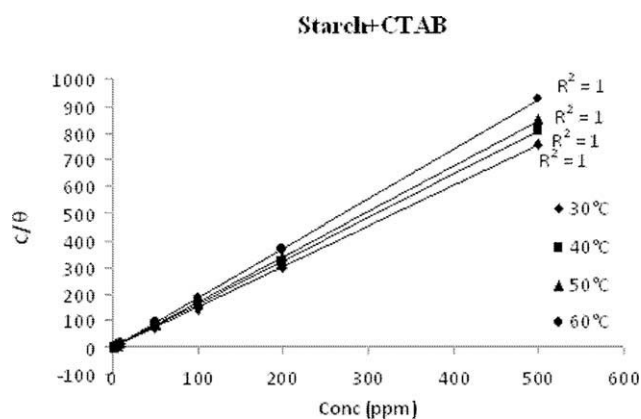


Figure 6 Langmuir adsorption isotherm for (starch + 1 ppm CTAB) adsorbed on mild steel surface in 0.1M H₂SO₄ at different temperatures.

interface obeys Langmuir adsorption isotherm at all the temperatures studied.

Effect of temperature

The corrosion of mild steel was studied in the temperature range of 30–60°C in the absence and presence of starch, surfactants and starch in combination with the surfactants. The logarithm of corrosion rate (log CR) versus reciprocal of absolute temperature (1/T) for 0.1 M H₂SO₄ is presented in Figure 7 for blank, starch, surfactants and starch-surfactant mixtures. Linear plot was obtained which indicates that it follows Arrhenius equation³⁷ given by relationship:

$$\log CR = \log A - \frac{E_a}{2.303 RT} \quad (6)$$

where CR is the corrosion rate, A is the Arrhenius constant, E_a is the apparent activation energy, R is the molar gas constant and T is the absolute temperature. The values of E_a obtained from the slope of the linear plot are presented in Table IV. The increases in E_a values in presence of the additives compared to the blank indicate the decrease in adsorption process of the inhibitor on the mild steel surface with rise in temperature and a corresponding increase in reaction rate

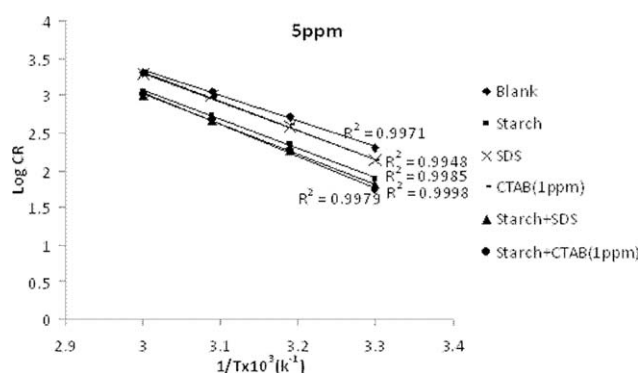


Figure 7 Adsorption isotherm plot for log CR versus 1/T in the absence and presence of starch, SDS, CTAB, and starch in combination with SDS/CTAB.

of greater area of metal that is exposed to acid.³⁸ This shows physical adsorption.³⁹

Enthalpy of adsorption, ΔH and entropy of adsorption, ΔS for the corrosion of mild steel in 0.1M H₂SO₄ in the presence of starch, surfactants and starch-surfactant mixtures was obtained by the equation:

$$CR = \frac{RT}{Nh} \exp\left(\frac{\Delta S}{R}\right) \exp\left(-\frac{\Delta H}{RT}\right) \quad (7)$$

where N is the Avogadro's number, h is the Planck's constant, R is the molar gas constant, and T is the absolute temperature. Figure 8 shows the plot of $\log (CR/T)$ versus $1/T$ for blank, starch and starch in combination with surfactants. Linear plot was obtained and from the slope $(-\frac{\Delta H}{2.303 R})$ and intercept $[\log(\frac{R}{Nh}) + (\frac{\Delta S}{2.303 R})]$ of the linear plot, the values of ΔH and ΔS , respectively were obtained. The calculated values are presented in Table IV. The enthalpy of adsorption increases in presence of the additives compared to the free acid solution; this indicates physical adsorption. The values of ΔS are positive which indicates a decrease in the system order in the presence of additives.⁴⁰ Figure 9 shows the plot of $\log(\frac{\theta}{1-\theta})$ versus $1/T$ for starch and starch in combination with the surfactants. Linear plot was obtained and from the slope $[\frac{-Q}{2.303 R}]$ of the linear plot, heat of adsorption, Q_{ads} was obtained. The

TABLE IV
Calculated Values of Kinetic/Thermodynamic Parameters for Mild Steel in 0.1M H₂SO₄ in the Absence and the Presence of Starch and Starch-Surfactant Mixtures from Weight Loss Measurement

Additives	Conc. 5ppm	E_a (kJmol ⁻¹)	ΔH (kJmol ⁻¹)	ΔS (kJmol ⁻¹ k ⁻¹)	Q (kJmol ⁻¹)	ΔG_{ads} (kJmol ⁻¹)			
						30°C	40°C	50°C	60°C
Blank	–	64.98	62.36	5.19	–	–	–	–	–
SDS	5	72.76	70.19	27.79	–51.20	–22.76	–21.14	–15.28	–9.96
CTAB	1	72.76	70.19	27.79	–37.74	–32.57	–29.39	–26.29	–20.31
Starch	5	74.50	71.90	28.55	–17.73	–33.54	–32.05	–31.07	–28.72
Starch + SDS	5 + 5	76.89	74.27	34.68	–19.84	–34.87	–33.39	–32.22	–30.54
Starch + CTAB	5 + 1	81.85	79.23	50.00	–27.30	–35.54	–34.56	–32.91	–14.95

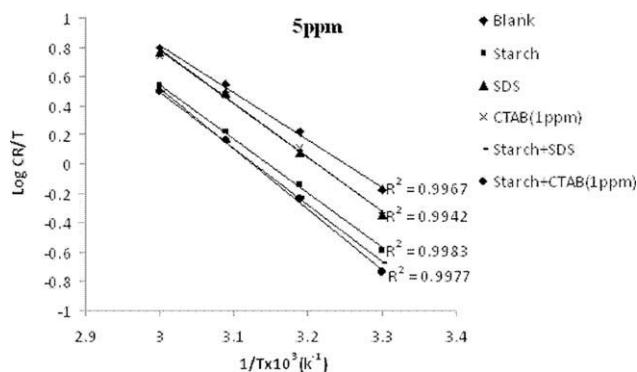


Figure 8 Adsorption isotherm plot for $\log CR/T$ versus $1/T$ in the absence and presence of starch, SDS, CTAB, and starch in combination with SDS/CTAB.

calculated values of Q_{ads} were negative (Table IV) indicating that the adsorption of starch, SDS, CTAB, and starch-surfactant mixture on mild steel surface is exothermic.⁴¹ In general, the values are less than -40 kJ mol^{-1} suggesting the physical adsorption of the compounds.⁴²

Free energy of adsorption, ΔG_{ads} was obtained from the intercept of plot of $\log (\% \text{ IE})$ versus \log inhibitor concentration ($\log C$) and evaluated using the following equation.

$$\log C = \log \left(\frac{\theta}{1-\theta} \right) - \log B \quad (8)$$

where, $\log B = -1.74 - \left(\frac{\Delta G_{ads}}{2.303RT} \right)$ and C , is the concentration of the system studied. The calculated values of ΔG_{ads} from 30 to 60°C for the various systems studied are presented in Table IV. The ΔG_{ads} values obtained are negative, which indicate the spontaneous adsorption of the starch and starch in combination with surfactants on the mild steel surface. The value of ΔG_{ads} of -40 kJ/mol is usually accepted as a threshold value between chemisorptions and physisorption. The values of ΔG_{ads} obtained in this study are below -40 kJ/mol (between -9.96 and -35.54 kJ/mol). This

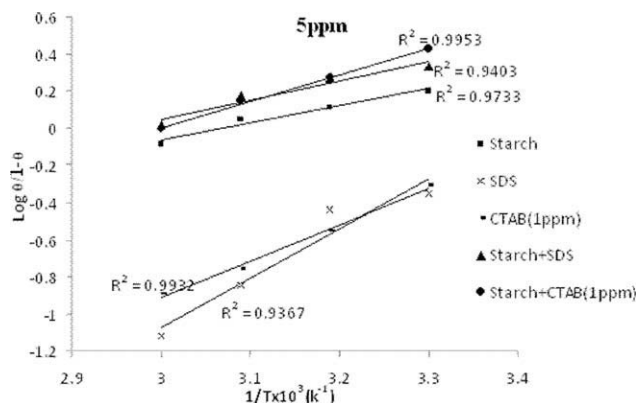


Figure 9 Adsorption isotherm plot for $\log (\theta/1-\theta)$ versus $1/T$ in the absence and presence of starch, SDS, CTAB, and starch in combination with SDS/CTAB.

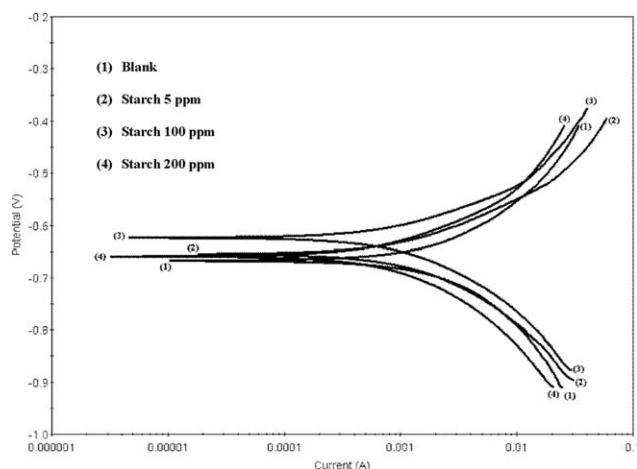


Figure 10 Potentiodynamic curves for mild steel in $0.1M \text{ H}_2\text{SO}_4$ in the absence and presence of various concentration of starch (1) Blank, (2) Starch 5 ppm, (3) Starch 100 ppm, and (4) Starch 200 ppm.

is consistent with electrostatic interactions between the charged molecules and the charge metals, which are indicative of physical adsorption.

Potentiodynamic polarization measurements

The potentiodynamic polarization curves for the corrosion of mild steel in $0.1M \text{ H}_2\text{SO}_4$ in absence and presence of varying concentration of starch and starch in combination with 5 ppm of SDS and 1 ppm of CTAB are shown in Figures 10 and 11. The values of electrochemical parameters as deduced from these curves, e.g., corrosion potential (E_{corr}), corrosion current density (i_{corr}), the anodic tafel slope (β_a), the cathodic tafel slope (β_c), corrosion rate and % IE are shown in Table V.

The study of electrochemical data (Table V) reveals that the value of i_{corr} continuously decreases in

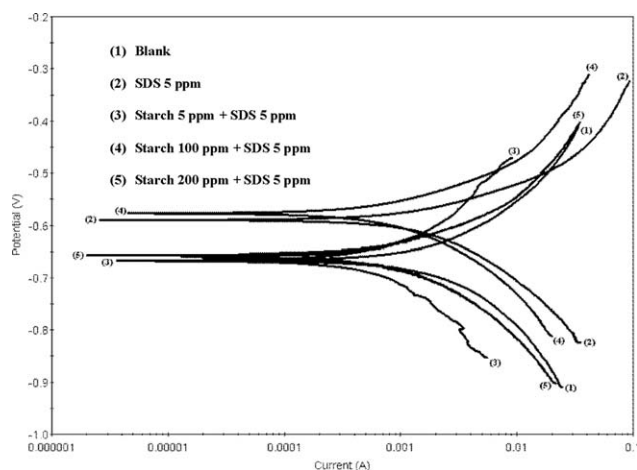


Figure 11 Potentiodynamic curves for mild steel in $0.1M \text{ H}_2\text{SO}_4$ in the absence and presence of various concentration of additives (1) Blank, (2) SDS 5 ppm, (3) Starch 5 ppm + SDS 5 ppm, (4) Starch 100 ppm + SDS 5 ppm, and (5) Starch 200 ppm + SDS 5 ppm.

TABLE V
Potentiodynamic Polarization Parameters for Corrosion of Mild Steel in 0.1M H₂SO₄ in the Absence and the Presence of Various Concentration of Starch and Starch-SDS Mixtures at 30°C

Additives	Conc. (ppm)	E_{corr} (mv)	I_{corr} (μA)	β_a (mV)	β_c (mV)	CR (mpy)	(%IE)
Blank	Blank	-667.318	4194.00	265.164	301.354	382.70	-
SDS	5	-589.965	3458.00	165.884	237.081	319.70	17.55
Starch	5	-655.000	1906.00	158.690	194.560	174.30	54.55
Starch	100	-623.892	1850.00	167.666	204.066	169.20	55.89
Starch	200	-658.905	1604.00	188.320	221.253	151.80	61.75
Starch + SDS	5 + 5	-667.347	1587.00	257.634	351.972	145.90	62.16
Starch + SDS	100 + 5	-577.109	1983.00	181.419	229.033	183.30	52.72
Starch + SDS	200 + 5	-659.277	1754.00	179.350	215.878	161.30	58.18

presence of starch. The maximum IE of about 61.75% was observed at a concentration of 200 ppm indicating that a higher coverage of starch on steel surface is obtained in the solution with highest concentration of inhibitor. The values of E_{corr} shifts to more positive value compared to the blank, indicating that starch acts more anodic than cathodic inhibitor. The addition of 5 ppm of SDS to varying concentration of starch improved the IE of starch significantly. However, the effect of SDS is more pronounced at lower concentrations of starch. The results as obtained by electrochemical studies are consistent with the results of the weight loss measurements.

CONCLUSIONS

1. Starch showed good performance as corrosion inhibitor for mild steel in 0.1M H₂SO₄ which is further improved in presence of surfactants SDS and CTAB. The effect of surfactants on corrosion inhibition behavior of starch appears to be synergistic in nature. Phenomenon of physical adsorption is proposed from the trend of IE with temperature.
2. The data obtained from weight loss measurements suggest corrosion inhibition by adsorption mechanism and fit well the Langmuir adsorption isotherm at all the concentrations and temperatures studied.
3. The results of potentiodynamic polarization measurements show that starch acts more anodic than cathodic inhibitor. The results are consistent with the results of the weight loss measurements.

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