Synergistic effect of l-proline mixed with sodium benzoate as sustainable corrosion inhibitor for mild steel in 1M HCl: Experimental and theoretical studies

Mosarrat Parveen

Corrosion Research Laboratory, Department of Applied Chemistry, Faculty of Engineering and Technology, Aligarh Muslim University, Aligarh, 202002-India
email id: mosarrat7parveen@gmail.com

Mohammad Mobin

Corrosion Research Laboratory, Department of Applied Chemistry, Faculty of Engineering and Technology, Aligarh Muslim University, Aligarh, 202002-India

ABSTRACT

Inhibition effect of L-proline (LPr) and LPr mixed with sodium benzoate (Lpr + NaBenz) on mild steel (MS) corrosion in 1M HCl at temperature 30°C was studied employing gravimetric method, electrochemical impedance spectroscopy (EIS), potentiodynamic polarization measurements and scanning electron microscopy (SEM). The concentration of Lpr was varied between 100-600 ppm. LPr inhibited the corrosion rate of MS at a considerable extent. Inhibition efficiency of LPr was synergistically enhanced on adding NaBenz at all concentrations. The change in impedance parameters indicated that LPr and Lpr+NaBenz molecules acted by adsorption at the MS/solution interface. Typically different surface morphologies for uninhibited and inhibited MS specimens verified the formation of adsorbed protective covering the MS surface. LPr alone and in combination with NaBenz acted as mixed type inhibitor and adsorbed on the MS surface in accordance with the Langmuir adsorption isotherm.

Keywords: *Mild Steel; Corrosion Inhibition; L-proline; Sodium Benzoate; Synergistic effect;*

INTRODUCTION

As one of the important metals in the world, mild steel (MS) is widely used in various petroleum and machinery industries due to its perfect mechanical workability, good availability, and affordability [1,2]. In these industries, to prevent the oxidation and corrosion after several working cycles, acid cleaning treatment is frequently used. However, this cleaned mild steel surface has been corroded by aggressive ions during the cleaning treatment itself. To overcome this problem inhibitor is mixed to acid solutions. Therefore, the use of many heterocyclic organic compounds having multiple bonds, aromatic rings or their hetero atoms like nitrogen, oxygen, sulfur etc. or is one of the most acknowledged practical methods for corrosion protection of metallic corrosion in acidic media, as well as for reduction of acid consumption occurring during the course of corrosion is well recognized since long time. Corrosion inhibitors efficiently reduce the undesirable destructive effect and prevent metal dissolution. These inhibitors prevent metallic corrosion by adsorbing on the active sites of steel and prevent its exposure to the corrosive environment. The adsorption process depends on structure of inhibitor and nature of corrosive environment. However most of these compounds used as corrosion inhibitors are expensive and hazardous to living beings. Because of economic and environmental factors, an inhibitor must not only be efficient but also cheap, nontoxic and innocuous in the environment. Various amino acids containing π electrons and heteroatoms in their molecules satisfy these criteria and thus proving amino acids as a potential source of new corrosion inhibitors [3]. Through these adsorption sites they are either adsorbed or form insoluble metal complex at the metal surface and inhibit metal corrosion.

Synergistic inhibition, which is an improved performance of a mixture of inhibitors compared with the individual inhibitors in preventing the corrosion of metals, has proved to be an effective method to improve the inhibition performance or to decrease the required dosage of the inhibitor and to expand the application of the inhibitor in acidic media [4,5].

In the present paper the authors are reporting the corrosion inhibition performance of LPr and NaBenz for MS in 1M HCl at temperature 30-60°C using, potentiodynamic polarization, weight loss, SEM.

EXPERIMENTAL PROCEDURE

MATERIAL, SOLUTION AND INHIBITOR PREPARATION

Chemical composition of mild steel, as analysed by optical emission spectrometer, (in weight %) chosen in the present investigation was 0.20 C, 0.53 Mn, 0.036 Si, 0.11 S, 0.098 P, and the remainder Fe. Dimension of working electrode for electrochemical experiments is 1.0 cm^2 whereas, rectangular specimens of dimension 2.5 × 2.0 × 0.03 cm with exposed surface area of 10.27 cm^2 were used during gravimetric studies. Specimens were abraded with a series of emery papers (grade 320-1200), degreased with 1:1 ethanol/water mixture, rinsed with double distilled water and finally dried in warm air and used with no further storage. L-proline (Pyrrolidine-2-carboxylic acid), molecular mass 115.13 g $mole^{-1}$], and NaBenz were used as received. Experiments were carried out in unstirred aerated 1M HCl solutions without and with various concentrations of LPr (100-600 ppm) and fixed concentration (10ppm) of NaBenz. All solutions were made using double distilled water.

WEIGHT LOSS MEASUREMENT

The metallic coupons after surface preparation were accurately weighed and immersed in 200 ml of 1M HCl solution without and with different concentrations of inhibitor for 6 h at temperatures 30-60°C. After desired period of immersion the coupons were taken out, the corrosion products formed on the steel surface were removed mechanically by scrubbing gently with bristle brush, washed, dried and final weight was recorded. The corrosion rate (v, mg cm^{-2} h^{-1}), inhibition efficiency (η_{w}, %) and surface coverage (θ) were calculated using the following relation

$$v = \frac{w_1 - w_2}{AT}$$

(1)

$$\eta_{w}\,(\%) = \frac{v_o - v_i}{v_o} \times 100$$

(2)

where A: is the area of the low carbon steel specimen (cm^2); and T: is the exposure time (h).

To judge that effect of NaBenz on corrosion inhibition behaviour of LPr is synergistic in nature, synergism parameter, S_θ was calculated using the following relation initially proposed by Aramaki and Hackerman[6] :

$$S_\theta = 1\text{-}\theta_{1+2} / 1\text{-}\theta'_{1+2} \qquad (3)$$

$$\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1\theta_2) \qquad (4)$$

where, θ_1 and θ_2 is surface coverage by LPr and NaBenz, respectively and θ'_{1+2} is measured surface coverage by both the LPr and NaBenz. In general, $S_\theta > 1$ indicates a synergistic effect whereas $S_\theta < 1$ implies that antagonistic behaviour prevails, which may lead to competitive adsorption.

ELECROCHEMICAL MEASUREMENTS

Electrochemical measurements (EIS and potentiodynamic polarization) were carried out in an Autolab electrochemical cell having three compartments for working, counter and reference electrodes. Ag/AgCl electrode (saturated KCl) was used as reference electrode and all the potentials given in the present paper are referred to this reference electrode. A Luggin-Haber capillary was included in the cell with its tip very close to the surface of the working electrode to minimize IR drop. The experiments were conducted at 30 ± 2°C using a temperature-controlled water bath. The volume of test solution was kept constant during each experiment. Before starting the measurements, the specimen was left in the test solution for 1 h to attain a steady state open circuit potential. Experiments were performed on Autolab Potentiostat/Galvanostat, model 128N with inbuilt impedance analyser FRA2 module connected to a personal computer.

EIS measurements were implemented at open circuit potential within frequency range of 10^{-2} to 10^{5} Hz with 10mV perturbation. Inhibition efficiency was calculated from the measured charge transfer resistance (R_{ct}) values using the following equation:

$$(\%\eta_{\mathrm{Rct}}) = \frac{Rct - Rct^{o}}{Rct} \times 100$$

(5)

where, R_{ct} and R_{ct}° are the charge transfer resistance in presence and absence of inhibitor, respectively. Potentiodynamic polarization measurements were performed at a scan rate of 0.00166 V/s in the potential range of 0.250V below the corrosion potential to 0.250V above the corrosion potential with reference to open circuit potential. The linear segments of the anodic and cathodic curves were extrapolated to the corrosion potential to obtain the corrosion current densities (i_{corr}). The measured i_{corr} values were used to calculate inhibition efficiency using the following equation:

$$\%\eta_{\mathrm{i_{corr}}} = \frac{i_{\mathrm{corr}}^{0} - i_{\mathrm{corr}}}{i_{\mathrm{corr}}^{0}} \times 100$$

(6)

where, i°_{corr} and i_{corr} are the corrosion current density in the absence and presence of inhibitor.

SURFACE ANALYSIS OF SPECIMEN

A scanning electron microscope (SEM) (Model: JEOL JSM-6510LV) was used to record surface morphology of the MS specimen corroded in 1M HCl solution in absence and presence of inhibitor at 30°C. For SEM studies MS surface was prepared by immersing in 1M HCl solution in absence and presence of 500 ppm of LPr, LPr (500 ppm) +NaBenz (10 ppm) at 30°C. After 6 h of immersion the specimens were retrieved, thoroughly washed with distilled water, dried in air and examined under SEM.

RESULTS AND DISCUSSION

WEIGHT LOSS MEASUREMENT

The corrosion parameters of MS in 1M HCl without and with varying concentrations of LPr or LPr+10 ppm NaBenz was evaluated using weight loss technique. To observe the effect of temperature the weight loss studies were performed at temperatures 30, 40, 50 and 60°C and the results are listed in Table 1. Data in Table 1 suggest the inhibitor LPr was acting as temperate corrosion inhibitor for MS corrosion in 1M HCl solution, the inhibition efficiency of inhibitor being both concentration and temperature dependent. The increase in LPr concentrations caused an increase in inhibition efficiency till it reached a maximum value of 82.5% at LPr concentration of 500 ppm at 30°C, a further increase in LPr concentration resulted in a little lowering of the inhibition efficiency (81.8%) due to desorption of some of the LPr molecules. However, an increase in temperature resulted in the lowering of inhibition efficiency at all the studied concentrations, suggesting physical adsorption. The weak Vander Waal's forces responsible for such type of adsorption tend to diminish at elevated temperatures.

Table 1: Corrosion parameters for mild steel in 1M HCl in absence and presence of different concentrations of LPr+10 ppm NaBenz additives at 30-60 °C from weight loss measurements.

LPr Conc.(ppm)	NaBenz Conc. (ppm)	Inhibition efficiency, η_w (%)			
		30°C	40°C	50°C	60°C
Blank	-				
100	-	65.8	58.2	56.2	53.3
200	-	72.4	68.0	67.2	58.5
300	-	79.8	71.0	70.0	62.3
400	-	80.9	75.3	74.0	64.0
500	-	82.5	77.3	75.2	66.7
600		81.8	76.4	70.2	61.4
-	10	3.5	5.7	7.9	9.9
100	10	70.3	62.3	60.6	58.0
200	10	78.1	76.3	73.1	65.2
300	10	82.9	79.2	75.7	70.7
400	10	86.7	82.6	79.9	75.8
500	10	96.9	85.2	82.5	72.7
600	10	95.9	77.6	73.4	69.4

The corrosion inhibition behaviour of LPr at temperatures 30-60°C was also examined in presence of small concentration of NaBenz and the results are depicted in Table 1. The presence of 10 ppm NaBenz further enhanced the inhibition efficiency of LPr at all the studied concentrations and temperatures. The maximum inhibition efficiency of 82.5% exhibited by LPr at 500 ppm at 30°C was increased to 96.9% in presence of NaBenz. The observed increase in inhibition efficiency is more than either of LPr or NaBenz alone indicating a synergistic effect between LPr and NaBenz.

Table 2: Values of synergism parameter, S_θ at different concentrations of LPr and varying temperature.

LPr Conc. (ppm)	NaBenz Conc. (ppm)	Synergism Parameter (S_θ)			
		30°C	40°C	50°C	60°C
100	10	1.11	1.05	1.02	1.00
200	10	1.21	1.27	1.13	1.07
300	10	1.14	1.32	1.14	1.16
400	10	1.38	1.33	1.19	1.34
500	10	5.25	1.45	1.31	1.10
600	10	4.28	0.99	1.03	1.13

Values of synergism parameter (S_θ) calculated for LPr and NaBenz at 30-60°C were all greater than unity (Table 2) indicating that the increased inhibition efficiency of Tyr resulting from the addition of NaBenz was synergistic in nature and proves that addition of a very small concentration of NaBenz can significantly improve the adsorption of LPr on the MS surface.

Electrochemical impedance spectroscopy

Nyquist plots and Bode diagrams for different concentrations of LPr, LPr and NaBenz in 1M HCl at 30°C were obtained and presented in Figure 2. The Nyquist plots show single capacitive loop, which is attributed to the charge transfer of the corrosion process. The diameter of the loops increased with increasing LPr concentration. The addition of NaBenz further caused an increase in the diameter of the circle. The capacitive loops are not exact semi circles but depressed to some extent, which is attributed to the frequency dispersion effect due to roughness and inhomogeniety of electrode surfaces. The increased diameter of capacitive loop in presence of NaBenz in comparison with the LPr alone indicated that impedance of LPr inhibited substrate increased with the addition of NaBenz. The notable point is that in presence of inhibitor, the Nyquist plots are similar and this means that protection mechanism did not change during the whole process.

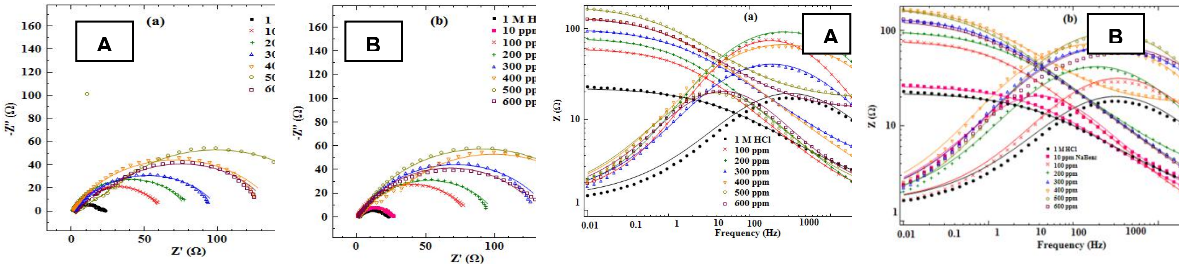

Figure 2: Nyquist plots and corresponding Bode modulus and Bode phase angle diagrams for mild steel in 1M HCl solution at 30˚C (A) with varying concentrations of LPr and (B) LPr mixed with NaBenz.

The Equivalent circuit (not shown here) includes solution resistance, R_s and double layer capacitance, C_{dl}, which is placed in parallel to charge transfer resistance, R_{ct}. To get more accurate semicircle fit CPE is substituted for double layer capacitance, C_{dl} as metal/solution interface does not correspond to an ideal capacitor. Impedance of a CPE is given by the expression:

$$Z_{CPE} = \frac{1}{Y_o (j\omega)^n} \tag{7}$$

where Y_o is the magnitude of CPE, j is the imaginary number and is equal to the square root of -1, ω is the angular frequency in Rads^{-1} ($\omega = 2\pi f_{max}$) and n corresponds to the phase shift, which is related to the inhomogeneties of the double layer. For n = 0, Z_{CPE} represents a resistance with $R = Q^{-1}$, for n = 1 a capacitance with C = Q and for n = -1 an inductance with $L = Q^{-1}$. The C_{dl} for a circuit including CPE can be calculated using the equation :

$$C_{dl} = Y_o (\omega_{max})^{n-1} \tag{8}$$

where, $\omega_{max} = 2\pi f_{max}$ (f_{max} denotes maximum frequency at which the imaginary component of the impedance has a maximum).

Table 3: EIS parameters for corrosion of mild steel in 1 M HCl in absence and presence of LPrand LPr- NaBenz additives at 30ºC.

LPr Conc. (ppm)	NaBenz Conc. (ppm)	R_s (Ω cm^2)	R_{ct} (Ω cm^2)	CPE $Y_0 \times 10^{-3}$ ($\Omega^{-1}s^n$ cm^{-2})	CPE n	$C_{dl} \times 10^{-3}$ (μFcm^{-2})	η_R (%)
Blank	-	1.473	21.22	0.16	0.9935	0.155	-
100	-	1.21	60.428	0.151	0.9961	0.156	64.9
200	-	0.61	81.202	0.106	0.9956	0.148	73.8
300	-	3.05	96.79	0.098	0.9953	0.104	78.1
400	-	1.48	133.26	0.091	0.9958	0.962	84.1
500	-	17.11	156.29	0.081	0.9961	0.891	86.4
600		14.13	117.66	0.159	0.9963	0.080	81.9
-	10	1.18	21.9	0.155	0.9949	0.152	3.1
100	10	0.61	81.20	0.153	0.9956	0.15	73.9
200	10	3.05	96.79	0.106	0.9953	0.104	78.1
300	10	1.48	133.26	0.108	0.9958	0.106	84.1
400	10	17.10	156.29	0.118	0.9961	0.117	86.4
500	10	2.59	169.51	0.116	0.9959	0.114	87.5
600	10	0.60	138.64	0.120	0.9940	0.117	84.7

The main parameters obtained from EIS measurements are R_{ct} and C_{dl}. A decrease in C_{dl} values with accompanying increase in R_{ct} values, in general, suggest that corrosion inhibition performance of LPr or LPr mixed with NaBenz for MS in 1M HCl solution was due to the increased surface coverage as well as increased thickness of adsorbed layer.

The increased inhibition effect of LPr with increasing concentration or by the addition of NaBenz, as visualized by Nyquist plots, is further confirmed by the corresponding Bode diagrams. In Bode modulus diagram, for whole frequency range, the impedance modulus increased with increasing LPr concentration or addition of NaBenz, whereas in Bode phase angle diagram a more negative value of phase angle at high frequency was noticed with increasing LPr concentration or addition of NaBenz. An increase in the values of absolute impedance at low frequencies with increase in LPr concentrations or addition of NaBenz to the LPr indicates lower corrosion rates or higher protection of MS in inhibited acid solution. Further, more negative values of phase angle at high frequencies with increase in LPr concentrations or addition of NaBenz to the LPr indicates superior inhibitive behaviour at higher concentration of LPr or for LPr mixed with NaBenz.

POTENTIODYNAMIC POLARIZATION (PDP) MEASUREMENT

The polarization curves (current-potential relationship) for MS in 1M HCl without and with different concentration of LPr or LPr mixed with NaBenz are shown in Figure 4. Different electrochemical kinetic parameters deduced from polarization curves like, corrosion potential (E_{corr}), corrosion current density (i_{corr}), the cathodic Tafel slope (*bc*), and the anodic Tafel slope (*ba*) are shown in Table 4.

A comparison of polarization curves in absence and presence of LPr or mixed LPr and NaBenz suggest that except the gradual shifting of anodic and cathodic currents to lower values for whole the potential range other aspects of polarization curves remained unchanged. This again confirmed that almost no change in the corrosion mechanism occurred due to the addition of LPr or when NaBenz was mixed with LPr. Further, in presence of LPr or LPr and NaBenz the values of E_{corr} shift towards more positive (anodic) direction, with a magnitude less than 85 mV[7],, with respect to the blank MS sample suggesting that LPr, and NaBenz, in general, act as mixed type inhibitor with predominantly anodic effect

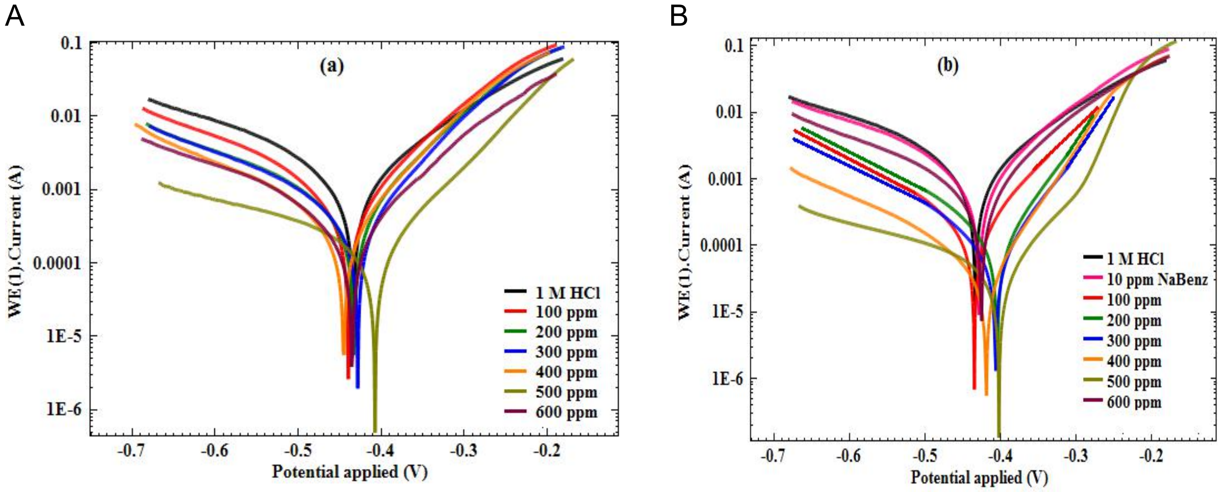

Figure 4: Potentiodynamic polarization curves for mild steel in 1M HCl solution at 30˚C (A) with varying concentrations of LPr and (B) LPr mixed with NaBenz.

The studied inhibitor affected the rate of cathodic hydrogen evolution reaction less than anodic metal oxidation reaction. The adsorption of LPr or LPr mixed with NaBenz inhibitor on the steel surface blocked both the anodic and cathodic sites. It is very clear from the table that the values of βa and βc without and with LPr or LPr + NaBenz do not show a significant difference indicating that both anodic and cathodic reactions were diminished by surface blocking effect of the adsorbed LPr or LPr + NaBenz. The values of η for LPr and LPr + NaBenz at each concentration were extremely high, and the maximum values of the efficiencies were 83.9% with 500 ppm LPr and 90.7% with LPr + 10 ppm NaBenz. It is obvious from the table that both Ecorr and icorr values of the inhibited systems were lower than that of the free acid solution. These results indicate that effectively protective film of inhibitor molecules formed on the copper surface thus blocked the active sites on the copper surface to protect corrosion of copper. Inhibition efficiency obtained by potentiodynamic polarization measurements are consistent with the one obtained by EIS.

Table 4: Potentiodynamic polarization parameters for corrosion of mild steel in 1M HCl in absence and presence of LPr and LPr + NaBenz additives at 30ºC.

LPr Conc. (ppm)	NaBenz Conc (ppm)	Ecorr (VvsAg/AgCl)	Icorr (µA/cm2)	ba/(V/dec)	bc/(V/dec)	%IE
Blank	-	-0.43	1.20	0.162	0.130	-
100	-	-0.440	0.436	0.111	0.084	63.7
200	-	-0.433	0.325	0.122	0.074	72.9
300	-	-0.431	0.277	0.118	0.076	76.9
400	-	-0.445	0.233	0.118	0.079	80.6
500	-	-0.422	0.192	0.288	0.102	83.9
600		0.435	0.218	0.131	0.089	81.8
	10ppm NaBenz	-0.433	1.141	0143	0.109	5.0
100	10	0.436	0.130	0.106	0.070	73
200	10	-0.405	0.107	0.107	0.069	77
300	10	-0.408	0.070	0.109	0.069	85.7
400	10	-0.405	0.06	0.242	0.077	87.6
500	10	-0.403	0.045	0.196	0.089	90.7
600	10	-0.414	0.092	0.119	0.067	81.1

SEM

Surface morphology of MS specimens prior to and after immersion in uninhibited and inhibited HCl solution were studied by means of SEM and the micrographs are shown in Fig. 6. In absence of inhibitor the steel surface was highly damaged due to the attack of corrosive HCl solution (Fig. 6a).

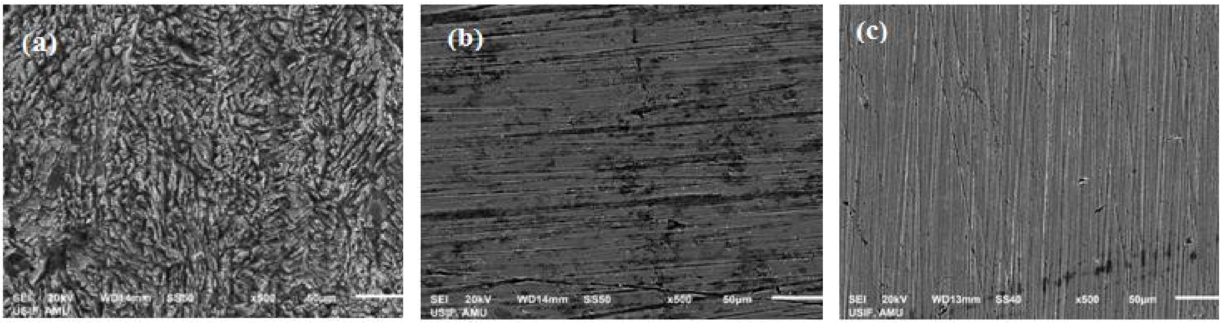

Figure 6: SEM image of mild steel in 1M HCl solution after 6 h immersion at 30°C (a) After immersion without inhibitor (c) with inhibitor LPr (d) with inhibitor LPr + NaBenz.

In presence of LPr the severity of the acid attack on the steel surface was suppressed due to the formation of a protective covering by the adsorbed LPr molecules (Fig. 6b). The surface smoothness is further improved when LPr is mixed with NaBenz (Fig. 6c).

CONCLUSIONS

- L-proline inhibited the corrosion rates of mild steel in 1M HCl solution to a considerable extent. Inhibition effect was both concentration and temperature dependent.
- Inhibition effect of L-proline was significantly enhanced on addition of small concentration of NaBenz. Effect of NaBenz appears to be synergistic in nature.
- Tafel polarization plots indicated that the L-proline or L-proline mixed with NaBenz acted as mixed-type inhibitors with predominantly anodic effect.
- SEM micrographs revealed that surface heterogeneity of mild steel was considerably reduced in presence of LPr and LPr mixed with NaBenz showing clear indication of their adsorption on steel surface and adequate protection in 1M HCl solution.

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