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Synergistic Inhibition of Corrosion of Mild Steel in Sulphuric acid by New Ternary System

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ABSTRACT

Corrosion inhibition of mild steel using a new ternary formulation, Urea, Zn (II) and L-Alanine in sulphuric acid medium at pH-4 was studied by weight loss and electrochemical studies. The inhibition efficiency increases with increasing concentration of inhibitors. The electrochemical impedance spectroscopy results showed that the change in the impedance parameters, Charge transfer resistance and double layer capacitance, is due to the adsorption of inhibitor molecules leading to the formation of a protective layer on the surface of the mild steel. The obtained results were confirmed by surface examination using Ultraviolet spectroscopy and Atomic Force Microscopy.

Keywords*:* Corrosion Inhibition, Mild Steel, Acid Solution, Impedance, AFM.

INTRODUCTION

Corrosion is the deterioration of metals and alloys by electrochemical reaction with its environment. It is a natural phenomenon which cannot be avoided, but it can be controlled and prevented using the suitable preventive techniques like metallic coating, anodic protection, cathodic protection and using inhibitors, etc. Inhibitors are playing a very major role in the process of corrosion control. Acid inhibitors are effectively used in metal finishing industries, pickling, cleaning, descaling, cleaning of boilers and heat exchangers [1]. Large numbers of organic compounds were studied to investigate their corrosion inhibition potential. Organic compounds containing Nitrogen, Sulphur and Oxygen atoms provide better corrosion inhibition.

In an attempt to develop a new environmentally friendly inhibitor combination, a new ternary system, Urea, Zn (II) and L-Alanine were chosen in the present study. The inhibitory effect of these ternary formulations on the corrosion of mild steel in H_2SO_4 (pH-4) was investigated by chemical and electrochemical techniques. The synergism exists between Urea - Zn^{2+} - L Alanine system was studied using the synergism parameters. The surface film formed on the metal surface was studied by UV and AFM.

MATERIALS AND METHODS

Molecular structure of Urea and L-Alanine is shown in Figure I .

Urea **L- Alanine**

Fig 1

The chemical composition of the mild steel used in the present study was S = 0.026% , P = 0.06%, Mn = 0.4% and rest iron, of the dimensions 1.0 X 4.0 X 0.2 cm were polished to a mirror finish and degreased with trichloroethylene and used for the weight-loss method and surface examination studies. The time of immersion was 24 hours and the volume of the solution is 100ml. The corrosion products were cleaned with Clark's solution [4].The cleaned samples weighed before and after immersion in acid solutions. From the determined weight loss values, the inhibition efficiencies (IE %), were calculated using the following equation,

$$IE = 100[1-(W_2 / W_1)]\% \qquad \text{--- (1)}$$

Where W_1 and W_2 are Corrosion rate in the absence and presence of inhibitor respectively.

The corrosion rate (CR) was calculated using the formula,

$$CR = 87.6W/DAT \qquad \text{--- (2)}$$

Where W = Weight loss in mg, D = 7.87 g/cm^3, A = Surface area of the specimen (10 cm^2), T = 24 hrs.

Synergism parameters are indications of synergistic effect existing between the inhibitors. S_I value is found to be greater than one suggesting that the existence of synergistic effect between the inhibitors [5-9].

$$s_I = \frac{1-\theta_{1+2}}{1-\theta'_{1+2}} \qquad \text{Where } \theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1 \theta_2)$$

θ_1 = Surface coverage of inhibitor Urea- Zn^{2+}
θ_2 = Surface coverage of inhibitor L-Alanine
θ'_{1+2} = Combined inhibition efficiency of inhibitor Urea - Zn^{2+}- L-Alanine

Where θ = surface coverage = IE % /100.

A CHI 660A electrochemical impedance analyzer model was used to record AC impedance measurements. A three electrode cell assembly was used. The working electrode was mild steel. A saturated calomel electrode (SCE) was used as the reference electrode and a rectangular platinum foil was used as the counter electrode. The exposed surface area was 1 cm^2. A time interval of 5 to 10 minutes was given for the system to attain a steady state open circuit potential. The real part (Z') and imaginary part (Z") of the cell impedance were measured in ohms for various frequencies. AC impedance spectra were recorded with initials *E*(v) =0 V, high frequency limit was 1×105 Hz, low frequency limit was 1 Hz, amplitude =0.005V and quiet time *t*q=2 s. The values of charge transfer resistance R_t and the double layer capacitance C_{dl} were calculated.

$$C_{dl} = ½ \, \pi R_t f_{max}$$

where f_{max} is maximum frequency.
UV-visible absorption spectra carried out using Cary Eclipse Varian (Model U.3400) spectrophotometer.

The surface morphology measurements of the mild steel surface were carried out by Atomic Force Microscopy (AFM) using SPM 2100 AFM instrument. Atomic Force Microscopy characterization is a powerful technique for the gathering of roughness information from a variety of surfaces.

RESULTS AND DISCUSSION

Weight – loss method:
The corrosion parameters such as inhibition efficiency (IE%) and corrosion rate (mm/y in presence and absence of inhibitors in H_2SO_4 (pH-4) are presented in Table 1.

Table 1: Corrosion rates (CR) of mild steel immersed in pH-4 sulphuric acid and the inhibition efficiencies (IE) obtained by weight loss method

Inhibitor system: 150 ppm Urea - 25 ppm Zn^{2+} + L-Alanine Immersion period: 1 day

Urea ppm	Zn^{2+} ppm	L-Alanine ppm	Corrosion Rate mm/y	I.E %	Surface Coverage(θ)	Synergism (S_I)
0	0	0	0.1947	---	--	--
0	25	0	0.1762	10	0.10	--
150	0	0	0.1297	33	0.33	--
150	25	0	0.0672	65	0.65	--
150	25	50	0.0371	81	0.81	1.34
150	25	100	0.0324	83	0.83	1.46
150	25	150	0.0301	84	0.84	1.49
150	25	200	0.0278	86	0.86	1.65
150	25	250	0.0231	88	0.88	1.86

Table 1 shows that 150 ppm of Urea has maximum IE 33% .When the first synergist Zn (II) is added. IE yet again increases. A maximum efficiency of 65% was obtained for the binary system containing 150 ppm of Urea and 25 ppm of Zn^{2+} ions. L- Alanine, an amino acid was added as the second synergist to enhance the inhibition efficiency [10].IE increases as the concentration of L-Alanine increases. This can be depicted from Figure 2. A combination of 150 ppm of Urea, 25 ppm of Zn^{2+} and 250 ppm of L-Alanine provides 88% inhibition efficiency [11]. This obviously suggests that combinations of these inhibitors inhibit the corrosion of mild steel to some extent. It is also observed from the table that the value of synergism parameter is greater than 1. So synergistic effect exists between Urea – Zn^{2+} and L- Alanine. Due to synergism, inhibition efficiency increases and corrosion rate decreases. Synergism may be due to the complex forming capability of Urea, Zn^{2+} and L- Alanine in solution.

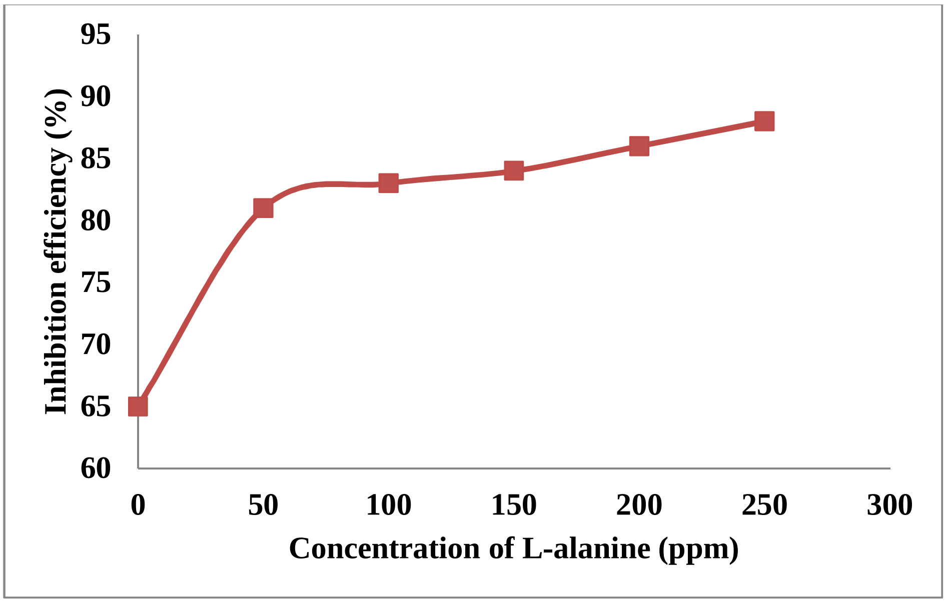

Figure 2. Inhibition efficiency of the ternary inhibitor formulation, Urea- Zn (II) -L-Alanine, as a function of concentration of L-Alanine, added to 150 ppm of Urea and 25 ppm of Zn^{2+} at pH 4.

Electrochemical impedance spectroscopy) measurements
The corrosion performance of mild steel in acid solutions in the absence and presence was also investigated using electrochemical impedance spectroscopy. Nyquist plot for mild steel in uninhibited and inhibited solutions are

shown in Figure 3 and the corrosion parameters are given in Table 2.It can be seen that the impedance of mild steel has markedly changed after the addition of inhibitors [12, 13]. It is clear that R_t increases and C_{dl} decrease in the presence of inhibitors. The decrease in C_{dl} and increase in R_t confirms the adsorption of the inhibitor forming protective adsorption layer [14, 15].

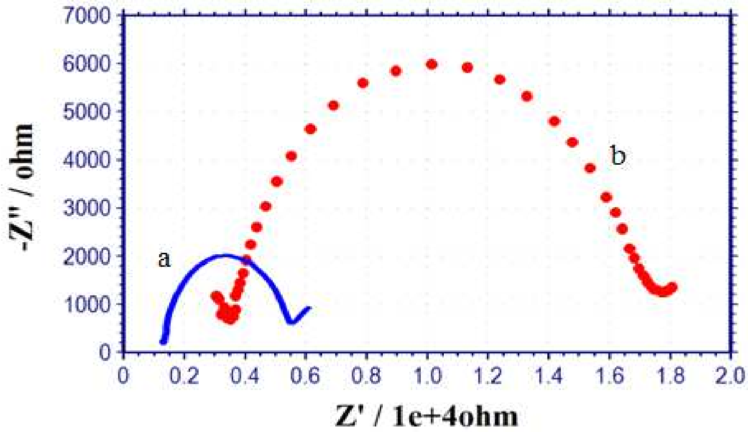

Fig.3. Nyquist plots of mild steel immersed in various test solutions.

a) Sulphuric acid at pH-4.
b) Sulphuric acid at pH-4 containing 150 ppm of Urea +25 ppm of Zn^{2+} + 250 ppm of L-Alanine.

Table 2 : Corrosion parameters of mild steel immersed in sulphuric acid solution at pH-4 in the absence and presence of inhibitors obtained AC impedance method.

Inhibitors	*R_t ohmcm^2*	*C_{dl} F/cm^2*	*Impedance value log (z/ohm)*
Blank	*4857*	*$3.9489x10^{-9}$*	*3.792*
150 ppm of Urea + 25 ppm of Zn^{2+} and 250 ppm of L-Alanine	*15041*	*$1.2752x10^{-9}$*	*4.259*

Analysis of UV – visible absorption spectra

UV-visible absorption spectra was used to validate the protective film formed on the metal surface [16 -17]. The UV-Visible absorption spectrum of an aqueous solution containing Urea- Fe^{2+} (Fig 4 a) shows a band at 348.0 nm with an absorbance 0.224 nm which corresponds to Fe^{2+} - Urea complex. When L-Alanine is added to the above - mentioned solution, the band shifted to 324 nm with an absorbance 0.611 nm which is shown in Fig 4 (b). There is a deviation in the absorbance values and their intensities. Change in position of the absorbance maximum and change in the value of absorbance indicate the formation of a complex between two species in solution [18]. This peak corresponding to Urea- Fe^{2+} and L-Alanine- Fe^{2+} complex. This complex is adsorbed on the metal surface and preventing the metal from further corrosion.

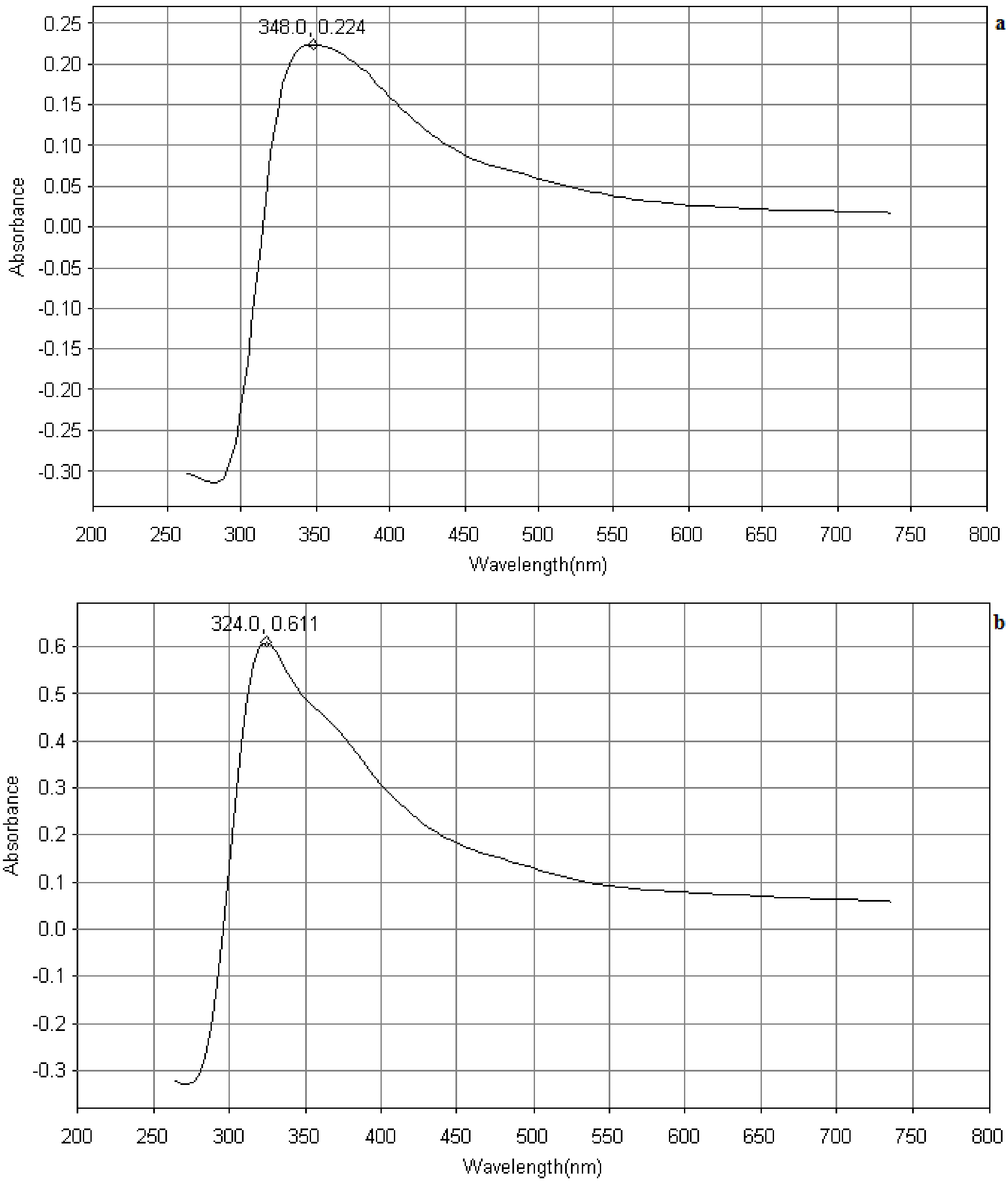

Fig.4.UV absorption spectra of solutions

(a) Urea - Fe^{2+} complex in solution
(b) Urea - Fe^{2+}, L-Alanine- Fe^{2+} complex in solution

Analysis of Atomic Force Microscopy Characterization

Atomic force microscopy is certainly the most adaptable and dominant microscopy technology for studying samples at the nanoscale. It gives an image in three-dimensional topography and also provides various types of surface measurements. AFM microscopy is a novel technique used to study the influence of inhibitor on the generation and the progress of the corrosion at the metal/solution interface [19, 20].

Fig 5 (a -c) displays the AFM images of polished metal, corroded surface in the absence of inhibitors and the smoothened surface in the presence of inhibitors, respectively. The relative roughness has been plotted in Fig 5 (d). Table 3 gives the corresponding roughness and peak-to-valley height values.

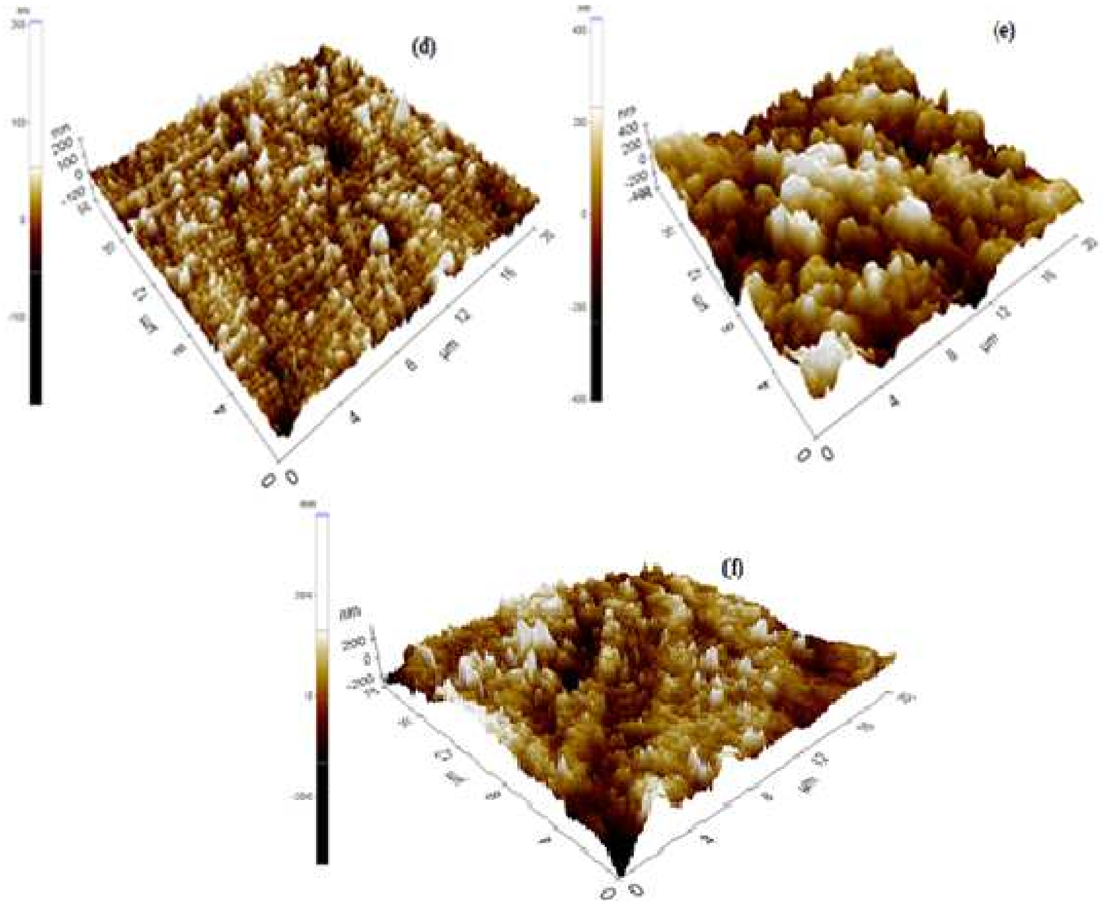

Fig. 5 3D AFM images of the surface of

a) Polished mild steel; b) Mild Steel immersed in pH-4 sulphuric acid solution; c) Mild steel immersed in pH-4 sulphuric acid solution in presence of inhibitors.

The average roughness (R_a), rms roughness (R_q) maximum peak-to-valley height (P-V) value for mild steel surface immersed in the different environment are displayed in table 3. It is inferred from the table that the value of R_q, R_a and P-V height values for the polished mild steel surface are 26.351 nm, 21.327 nm, and 129.754 nm respectively, which shows a more homogeneous surface. The slight roughness noted on the polished mild steel surface is due to the atmospheric corrosion.

For the corroded metal surface, the R_q, R_a and P-V height values for the mild steel surface immersed in sulfuric acid solution at pH-4 are 152 nm, 132 nm, and 584 nm respectively. These data suggests that mild steel surface immersed in sulphuric acid solution at pH-4 has a greater surface roughness due to the corrosion.

But in the presence of Urea, Zn^{2+} and L-Alanine, the smoother surface was obtained and the R_q, R_a and P-V height values are decreased to 52 nm, 44 nm, and 248 nm respectively nm . The reduction of these parameters established that mild steel surface becomes smoothened due to the deposition of inhibitors on the metal surface. The smoothness of the surface is due to the formation of a hard protective film of Urea- Fe^{2+} and L-Alanine - Fe^{2+}complex and $Zn(OH)_2$ on the metal surface thereby inhibiting the corrosion of mild steel.

Table.3 AFM Data for Mild Steel Surface Immersed in Inhibited and Uninhibited Environment

Sample	*RMS (R_q) Roughness(nm)*	*Average roughness(R_a) (nm)*	*Maximum peak-to-valley height (P-V) (nm)*
Polished Mild Steel	*26.351*	*21.327*	*129.754*
Without Inhibitor (Blank)	*152*	*132*	*584*
With Inhibitor system	*52*	*42*	*248*

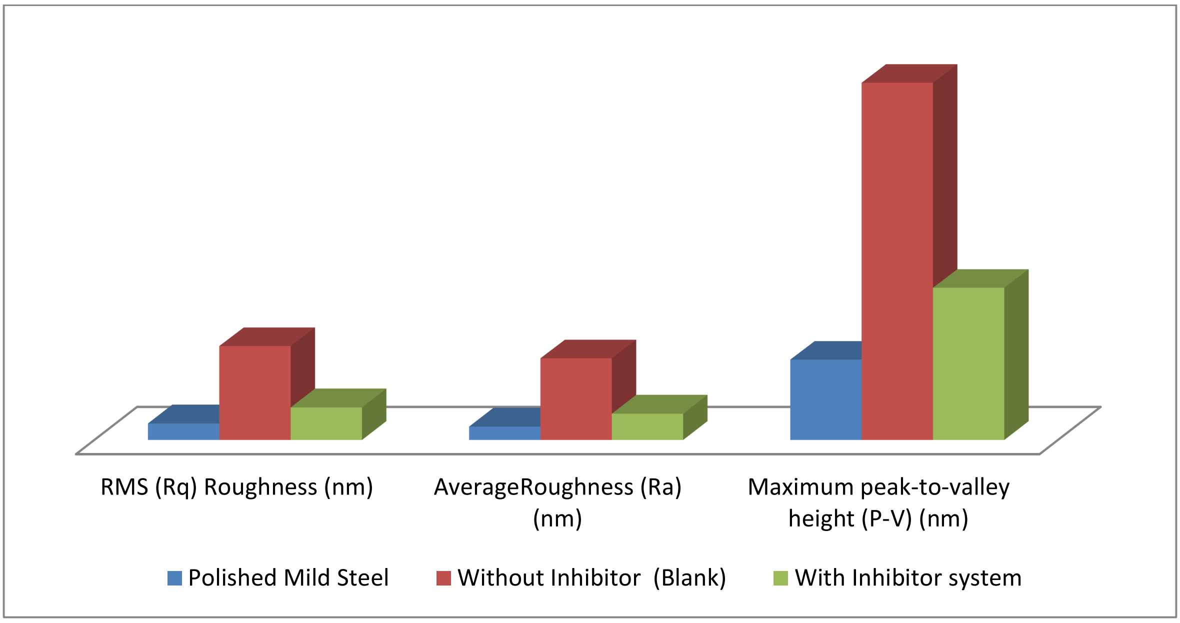

Fig.5 d Comparison of Rq, Ra and P-V values of the three systems.

CONCLUSION

The results of the weight-loss study show that the formulation consisting of 150 ppm of Urea and 25 ppm of Zn^{2+} and 250 ppm of L-Alanine has excellent inhibiting property in controlling corrosion of mild steel in the sulphuric acid solution at pH-4 for one - day immersion. A synergistic effect exists between Zn^{2+} - Urea – L- Alanine. AC Impedance, UV and AFM studies reveal that the protective film formed on the surface and thereby diminishing the corrosion rate.

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