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Histidine as Synergistic additive on Poly (N-Methyl Aniline) for mild Steel Corrosion in 0.5 M H_2SO_4

R. Menaka, M. Nandhini and S. Subhashini
Department of chemistry, Avinashilingam Institute for Home science and Higher Education University for Women

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Abstract

An inhibitor system composed of Poly(N-Methyl Aniline) [PNMANI] and histidine has been evaluated for its synergistic corrosion inhibition performance for mild steel in 0.5M H_2SO_4. PNMANI was prepared by free radical polymerisation using ammonium peroxodisulphate as initiator. 100ppm PNMANI exhibited 70% inhibition efficiency. In order to enhance the inhibitive action of PNMANI, histidine was added as a synergistic additive. The influence of histidine on PNMANI has been evaluated by weight loss and electrochemical methods. As expected, the inhibition efficiency gradually increased with increase in histidine concentration. The maximum inhibition efficiency of 89% was achieved for the inhibitor system viz 100ppm of PNMANI-130ppm of histidine. The enhanced inhibition performance of the inhibitor system has been proven thermodynamically.

Keywords: PNMANI, histidine, mild steel, synergism.

Introduction

Steel is widely used as the constructional material in most of the major industries particularly in food, petroleum, power production, chemical and electrochemical industries, especially due to its excellent mechanical properties and low cost. Mild steel undergo considerable dissolution when they are exposed to acid solutions or aggressive environment. The use of inhibitors is one of the most practical methods to prevent the corrosion or to reduce the corrosion rate. Organic inhibitors[1-3] containing hetero atoms like oxygen, nitrogen, sulphur and phosphorus etc shows better corrosion inhibition by forming protective film on the metal surface.

To improve the performance of organic corrosion inhibitor, extensive synergistic studies have been carried out. Synergism has become one of the most important effects in inhibition processes and serves as the basis for all modern corrosion inhibitor formulations. The synergistic inhibition effect of combination of organic compounds with certain metal cations[4-6] and halide anions[7-8] have also been reported.

The use of polymer as effective corrosion inhibitor for mild steel have drawn considerable attention due to their inherent stability and cost effectiveness. A number of polymers have been reported to inhibit the corrosion of mild steel in acid media. Poly(diphenyl amine), polyethylene glycol, polyvinyl alcohol, polyethylene glycol methyl ether are some of the reported polymers[9-13]. Polymeric compounds adsorb more strongly on the metal surface with their multiple adsorption sites. Their inhibition efficiency has been upgraded by addition of small amount of cations or anions which proves the existence of synergistic action. A series of reports highlighted the synergistic effect of halide ions on corrosion inhibition of metals by polymers[14-16]. The studies have also reported the effect of polymer- polymer mixtures or blends on corrosion inhibition of metals[17].

The present study is to investigate the synergistic effect of poly (N- methyl Aniline) and Histidine on the mild steel corrosion in acid medium. It was found that the inhibition efficiency was enhanced on adding aminoacid(Histidine) to the polymer (PNMANI). The present study reports on the corrosion inhibition effect of poly(N- methyl Aniline) –Histidine mixture for mild steel in H_2SO_4 using weight loss and electrochemical techniques.

Material and Methods

LR grade of L-Histidine and 98% Analytical grade of H_2SO_4 were used for the corrosion inhibition studies. LR grade of N-Methyl Aniline was used for the polymer synthesis. Mild steel sheet with composition of C=0.084%, Mn=0.207%, Si= 0.021%, P= 0.019%, S=0.012%, Cr=0.026%, Mo=0.029%, Ni=0.010% and remaining Fe was cut into rectangular pieces of area 1x5cm^2. The polished specimens were washed with distilled water, thoroughly dried and stored in a desiccator for weight loss measurements.

Synthesis of Poly(N-Methyl Aniline) PNMANI: 0.1 mole of distilled N-Methyl Aniline was dissolved in 100 ml of 1M hydrochloric acid. The solution was cooled at 0-5^o and 2% ammonium persulphate was added to the mixture with constant stirring. The reaction was continued for two hours and the

mixture is refrigerated for 24 hours. The polymer solution was neutralized with ammonium hydroxide. The polymer was precipitated using ethanol and then dried.

Weight loss measurement: Weight loss measurements were performed with the clean and dry rectangular strips. The mild steel strips were immersed in triplicates in 100 ml of 0.5 M H_2SO_4 in the absence and presence of 100ppm poly(N- methyl Aniline) and different concentrations (40-130ppm) of Histidine for different immersion periods at room temperature. At elevated temperatures, a constant immersion period of half an hour was selected and the studies were conducted for the same concentration of inhibitor mixture. The samples were washed, dried and reweighed. From the obtained weight loss, corrosion rate, inhibition efficiency (IE) and surface coverage(Θ) were calculated using following formulae,

$$CR(mpy) = \frac{534Wo}{DAt}$$

$$IE = \frac{Wo - Wi}{Wo} X\ 100$$

$$\Theta = \frac{Wo - Wi}{Wo}$$

Where, W_o and W_i are the weight loss of the coupon in the absence and presence of inhibitor, A is the area of the specimen in cm^2,D is the density of the material in g/cm^3, t is the time of exposure in hours.

Electrochemical measurements: Frequency Response analyzer (Solartron 1280B) supported with corrware and z- plot corrosion software was used for data acquisition and analysis. The conventional three- electrode system consisting of saturated calomel electrode (SCE) as reference electrode, platinum foil as counter electrode and MS strips having exposed area of 1 cm^2 as working electrode was used. The electrodes were immersed in 0.5 M H_2SO_4 solution for 30 minutes until a steady – state potential was reached. The polarisation studies were carried out over a potential range of 200mV to 1500mV with respect to reference electrode and its current response was measured at a scan rate of 1mV sec^{-1}. Anodic and cathodic tafel segments were extrapolated to obtain corrosion potential (E_{corr}) and corrosion current density (I_{corr}). The IE was evaluated using the following formula:

$$IE(\%) = 100\ X\ \left[1 - \frac{Icorr}{I°corr}\right]$$

Where, I_{corr} and I^o_{corr} are corrosion currents in the presence and absence of the inhibitor.

Impedance measurements were carried out at each corrosion potential. An AC sine wave of 10 mV amplitude is applied to the electrode and the frequency was varied from 10 kHz to 10 MHz. The real Z and the imaginary Z' were plotted in the Nyquist plot. From Nyquist plot, polarization resistance R_p, charge transfer resistance $R_{ct}$and double layer capacitance values $C_{dl}$are obtained,and IE were calculated using the following formulae.

$$IE(\%) = \frac{Rct - Rct°}{Rct} X100; \frac{Rp - Rp°}{Rp}\ X\ 100$$

Results and Discussion

Effect of Histidine on PNMANI: Weight loss measurements were carried out in 0.5 M H_2SO_4 in absence and presence of different concentrations of PNMANI to determine its inhibitive effect against corrosion. The inhibition behavior of PNMANI was found to be 70% at 100 ppm. In order to enhance the inhibition efficiency of PNMANI, various concentrations (40-130ppm) of histidine was added. The corrosion rate of mild steel samples in 0.5 M H_2SO_4 in presence of PNMANI with histidine were determined by weight loss measurements at different immersion time and concentration. The obtained results are shown in Figure figure 1 and 2. The inhibition efficiency was found to be affected by both time and concentration, and maximum efficiency of 89% was obtained for 130ppm Histidine+100ppm PNMANI after 3 hours of immersion. This may be due to adsorption of inhibitor molecules on the metal surface. A decrease in inhibition efficiency was observed for prolonged immersion i.e. after 3 hours till 24 hours which could be attributed to desorption of inhibitor from the metal surface.

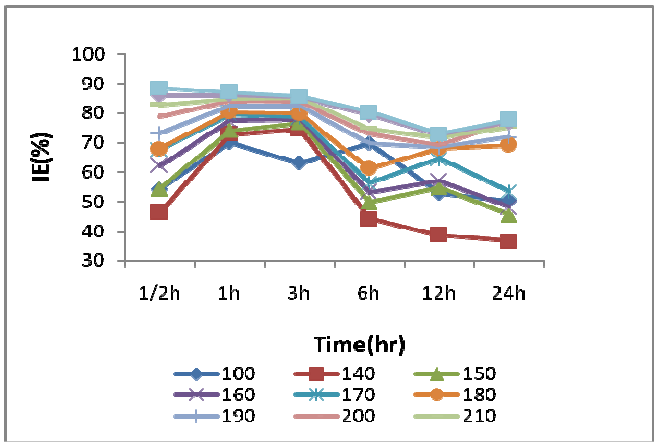

Figure-1
Effect of PNMANI-Histidine with immersion time

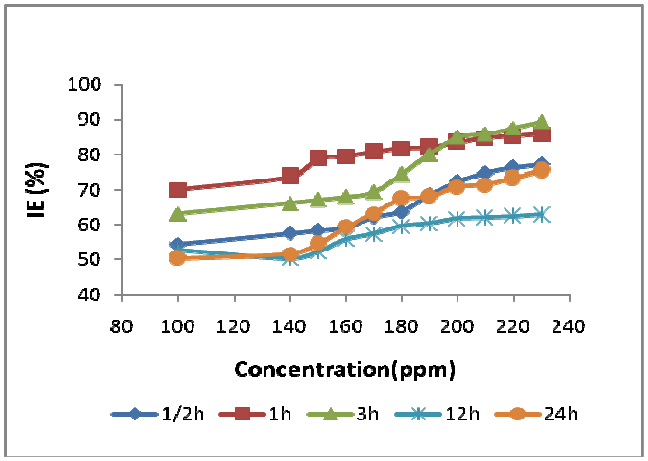

Figure 2
Variation of IE with concentration of PNMANI- Histidine

Synergism considerations: The mild steel corrosion in 0.5 M H_2SO_4 in absence and presence of different concentration of Histidine along with 100 ppm of PNMANI was studied. Addition of histidine concentration further enhanced the inhibition efficiency values (table 1). The synergistic inhibition effect was analyzed by estimating the synergism parameter (S_I) from inhibition efficiency obtained from weight loss method. According to Aramaki and Hackerman[18] (S_I) is calculated using the equation:

$S_I=1-I_{1+2}/1-I'_{1+2}$.

Where I_1 is the inhibition efficiency of histidine, I_2 is the inhibition efficiency of PNMANI, I'_{1+2} is the inhibition efficiency of PNMANI in combination with histidine. The values of S_I for PNMANI-histidine are found to be more than unity suggesting that enhanced inhibition efficiency caused by the synergistic action of histidine.

Effect of temperature: Temperature can modify the interaction between mild steel and inhibitor molecule in acid medium. Performance of PNMANI- Histidine system was studied for ½ hour of immersion at various temperatures in order to investigate the effectiveness and mechanism of inhibition. From the table 2, it can be seen that the corrosion rate increased with increasing temperature and the inhibition efficiency decreased with rise in temperature. A decrease in inhibition efficiency at elevated temperature may be attributed to physical adsorption of the inhibitor system[19]. At higher temperature, a decrease in inhibition efficiency may also due to desorption of inhibitor molecules.

Kinetic and Thermodynamic parameters of dissolution: Figure 3 shows the Arrhenius plot of log corrosion rate (CR) versus the reciprocal of absolute temperature (1/T). The apparent activation energy (Ea) was calculated by the following equation,

E_a= -2.303 *R*slope of the Arrhenius plot

Table-1
Synergism Parameters for 100ppm PNMANI with various concentrations of Histidine

IE of 100ppm PNMANI	Concentration of histidine (ppm)	IE of histidine (%)	IE of PNMANI-histidine (%)	Synergism parameter,S_I
63.2	40	30.51	66.26	1.420
	50	34.18	67.22	1.455
	60	36.11	68.03	1.466
	70	40.28	69.38	1.498
	80	41.04	74.36	1.407
	90	42.09	80.11	1.318
	100	47.43	84.87	1.307
	110	53	85.79	1.358
	120	54.9	87.57	1.352
	130	56.56	89.3	1.344

Table 2
Performance of PNMANI - Histidine at various temperatures

Concentration (ppm)		Temperature(K)											
		303		313		323		333		343		353	
		CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)
Blank		1107.68	-	4849.37	-	6642.08	-	16257.6	-	28224.0	-	29898.6	
PNMANI	Histidine												
100	-	505.87	54.33	1535.05	68.34	4299.89	35.3	9873.19	39.27	18333.4	35.04	18534.0	38.01
100	40	470.98	57.48	2407.24	50.35	3959.74	40.38	9515.59	41.46	18760.8	33.52	23418.3	21.67
100	50	462.26	58.26	2232.80	53.95	3863.80	41.82	9332.43	42.96	18734.6	33.62	22860.0	23.54
100	60	453.53	59.05	2215.36	54.31	3732.97	43.79	9201.60	43.40	18682.3	33.80	21787.3	26.42
100	70	418.65	62.20	2110.69	56.47	3663.19	44.88	9114.38	43.93	18664.8	33.86	22903.7	27.12
100	80	401.20	63.77	2075.81	57.19	3628.31	45.40	8599.79	47.10	17958.3	36.37	21516.9	28.03
100	90	348.87	68.50	1997.31	58.81	3410.54	48.65	8530.01	47.53	17740.3	37.14	22310.6	34.01
100	100	305.26	72.44	1613.55	66.72	3296.87	50.36	7954.37	51.07	16641.3	41.03	18595.0	37.80
100	110	279.10	74.80	1395.50	71.22	3078.83	53.67	7692.71	52.68	16414.6	41.84	18534.0	38.01
100	120	261.65	76.37	1378.06	71.58	3056.83	53.97	7682.61	52.74	16214.0	42.55	18411.9	38.41
100	130	252.93	77.16	1151.29	76.25	2952.72	55.54	7542.12	53.60	15708.1	44.34	16353.5	45.30

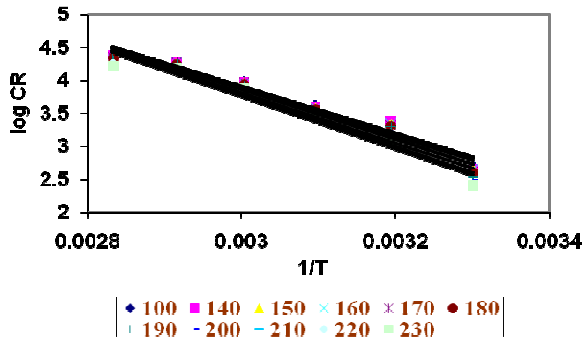

Figure-3
Arrhenius plot of PNMANI - Histidine

The values of Ea obtained from the slope of Arrhenius plot are listed in table 4. It can be seen from the table the Ea value (67.658 kJ/mole) in presence of PNMANI is higher than that in the acid solution (58.344 kJ/mole), and the E_a values are still higher in the presence of PNMANI along with different concentration of histidine. Hence the synergistic action of histidine on PNMANI is proved by increasing E_a values. The decrease in inhibition efficiency with increase in temperature and the increase of E_a values in presence of inhibitor system indicates the physical adsorption mechanism[20].

Table-3
Thermodynamic parameters of adsorption of PNMANI – Histidine

Concentration (ppm)		- ΔG (kJ / mole)					Change in enthalpy (−ΔH kJ / mole)	Change in entropy (ΔS kJ / mole)
		313 K	323 K	333 K	343 K	353 K		
Blank		-	-	-	-	-	-	-
PNMANI	**HISTIDINE**							
100	-	9.983447	13.99639	13.95924	14.89556	14.95364	18.3655	0.096111
100	40	12.82543	14.31937	14.63898	16.04771	18.27751	25.5861	0.12262
100	50	12.62934	14.34489	14.65974	16.2317	18.16614	25.6888	0.122942
100	60	12.75958	14.30208	14.78879	16.39281	17.90408	24.2987	0.118803
100	70	12.68981	14.34628	14.897	16.55808	17.97721	26.1815	0.124615
100	80	12.7622	14.4434	14.70119	16.40679	18.01123	25.586	0.122714
100	90	12.72981	14.23809	14.80314	16.46653	17.34767	25.0712	0.120567
100	100	11.97986	14.1921	14.55283	16.14652	17.01448	26.5007	0.123885
100	110	11.55885	13.96683	14.50934	16.19047	17.1315	29.5047	0.132681
100	120	11.63405	14.05935	14.63149	16.24013	17.21833	30.2681	0.135176
100	130	11.11803	14.00852	14.65894	16.1591	16.51626	28.4932	0.129093

Table-4
Activation parameters of PNMANI- Histidine in 0.5 M H_2SO_4

Concentration (ppm)		E_a kJ/mol	ΔH_a kJ/mol	ΔS_a J/mol	E_a-ΔH_a kJ/mol	RT kJ/mol
Blank		58.344	55.446	17.74	2.898	2.934
PNMANI	**Histidine**					
100	-	67.658	64.731	287.17	2.927	
100	40	68.329	65.400	400.24	2.929	
100	50	68.831	65.901	468.19	2.930	
100	60	68.565	65.635	415.84	2.929	
100	70	70.607	67.670	863.08	2.936	
100	80	70.084	67.149	685.97	2.934	
100	90	72.684	69.741	1713.53	2.946	
100	100	73.203	70.258	1845.44	2.944	
100	110	75.383	72.432	3868.35	2.951	
100	120	76.170	73.216	5071.79	2.953	
100	130	76.295	73.341	4953.64	2.954	

From the transition state theory, the graph of log CR/T vs. 1/T is plotted. From the plot the slope of $\Delta H_a/2.303R$ and an intercept of $\log R/Nh+\Delta S_a/2\text{-}303R$ were obtained, from which the values of $-\Delta H_a$and $-\Delta S_a$were calculated respectively and are tabulated (table 4). These values increase with increase in histidine concentration. The positive sign of the $-\Delta H_a$ reflect the endothermic nature of metal dissolution process[21]. The increase in the values of $E_a$and $-\Delta H_a$with increase in the concentration of histidine suggests the increase in energy barrier of metal dissolution reaction[22]. The higher values of E_a also indicate the higher protecting efficiency[23].

We state that $E_a$and $-\Delta H_a$values vary in the same manner with the inhibitor concentration. This can be used to verify the known thermodynamic relation between E_a and $-\Delta H_a$.

$$E_a-\Delta H_a=RT$$

The calculated values are very close to RT which is equal to 2.934 kJ /mole at 353 K[24]. The positive values of entropy in the absence and presence of inhibited system infers that the rate determining step for the activated complex is dissociation step rather than association. The increase in entropy is considered to be a driving force for the adsorption of inhibitor onto the metal surface.

Thermodynamic parameters of adsorption: The free energy of adsorption (ΔG_{ads}) was calculated using the equation,

$\text{Log } C = \text{Log } (\theta /1\text{-}\theta)\text{-Log } B$

$\text{Log } B = -1.74 - (\Delta G_{ads}/2.303\ RT)$

The (ΔG_{ads}) values are listed in Table 3 for the studied inhibitor system at different temperatures. The negative values of (ΔG_{ads}) indicate the spontaneous adsorption of the inhibitor system and its stability on the mild steel surface[25]. It can also be seen that the values of ΔG_{ads} slightly increase with inhibitor concentration and temperature. It is universally accepted that the values of ΔG_{ads} around $-20 kJmol^{-1}$ regarded as physisorption physical adsorption, which is due to electrostatic interaction between the charged molecules and the charged metal, and those values around -40 $kJmol^{-1}$ regarded as chemisorptions chemical adsorption, which is due to charge sharing or a transfer from the inhibitor molecule to metal surface forming a covalent bond[26-27]. In the present study, the free energy of adsorption (ΔG_{ads}) are found to be in the range of (9-16 $kJmol^{-1}$) indicating the spontaneous physical interaction between mild steel surface and the inhibitor system.

The thermodynamic functions of adsorption reaction $\Delta H_{ads}$and ΔS_{ads} were calculated from the plot of ΔG_{ads}vs T. The intercept and slope of the plot gives enthalpy of adsorption (ΔH_{ads}) and entropy of adsorption (ΔS_{ads}) respectively. The obtained ΔH_{ads} value is negative which indicates that the adsorption of inhibitor is an exothermic process[28]. For an exothermic process, physisorption is differentiated from chemisorption by the absolute values. When the ΔH_{ads} values are less than $40 kJmol^{-1}$it corresponds to physisorption, and if ΔH_{ads} is around $100 kJmol^{-1}$ it corresponds to chemisorption[29]. In this case the enthalpyof adsorption (ΔH_{ads}) values are less than $40 kJmol^{-1}$confirming the physical nature of adsorption[30]. The adsorption of inhibitor molecules is accompanied by positive values of ΔS_{ads}. This can also be attributed to the increase in solvent entropy which is due to desorption of water molecules and thereby causing the adsorption of the inhibitor on the metal surface[31].

Adsorption isotherms: Inspection of tables suggests that PNMANI- Histidineis an effective corrosion inhibitor for mild steel corrosion. The adsorption of the inhibitor is an essential step of the inhibition mechanism and it can provide information about the nature of metal-inhibitor interaction. The surface coverage (θ) is an important parameter in discussing the adsorption characteristics and it is calculated by,

$$\theta = \frac{\text{CR (blank)} - \text{CR (inhibitor)}}{\text{CR (blank)}}$$

By using θ values of different inhibitor concentrations, several adsorption isotherms like Langmuir,Temkin and Freundlich etc., were assessed. The plot of log θ/(1- θ) Vs. log C gave straight lines with slope values close to unity suggesting theadsorption of PNMANI in presence of Histidine obeys Langmuir isotherm figure 4.

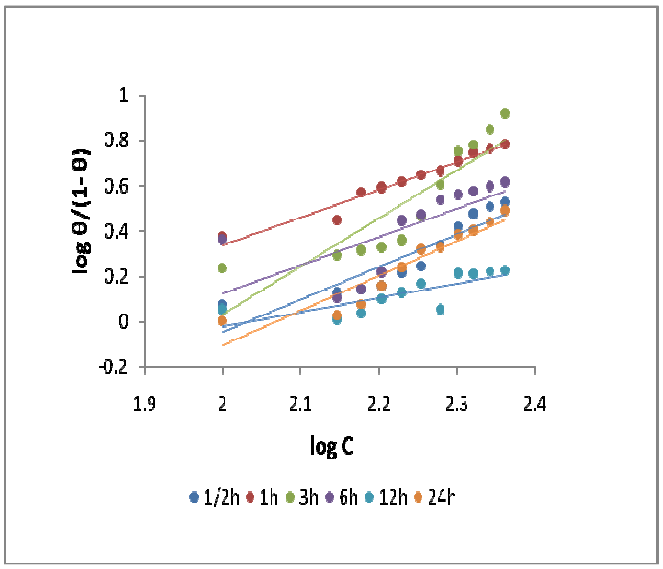

Figure-4
Langmuir adsorption isotherm for PNMANI-Histidine in 0.5M H_2SO_4

Potentiodynamic polarization measurements: The influence of histidine on PNMANI on the cathodic and anodic potentiodynamic polarization curves of mild steel in 0.5M H_2SO_4 is shown in figure 5. Electrochemical parameters such as Tafel slope (b_a and b_c), corrosion current (I_{corr}), corrosion

potential (E_{corr}) and inhibition efficiency (IE) are depicted in Table 5.From the table, the values of cathodic and anodic Tafel slopes show a marked change with inhibitor concentration indicating the mixed behavior of the inhibitor system[32]. The marginal shift in the E_{corr}value indicates that the mixed type inhibitor controlled both the cathodic and anodic reactions[33]. The I_{corr} values decreases with the increase in the inhibitor concentration thus by reducing the metal dissolution. These results are consistent with weight loss measurements.

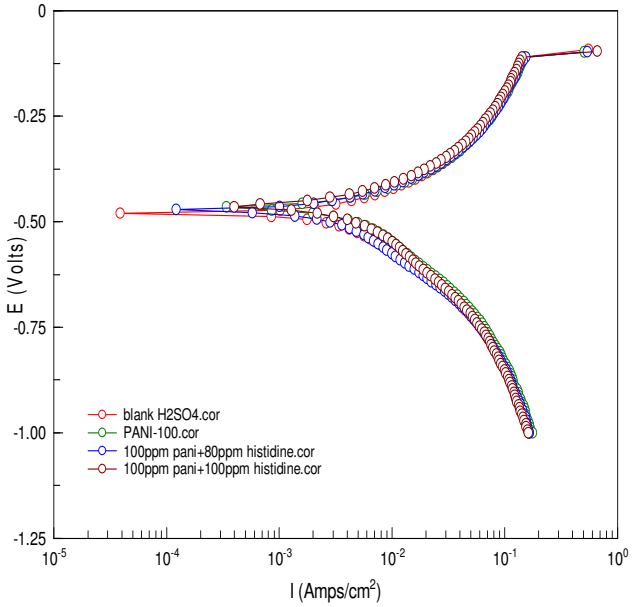

Figure-5
Polarization curves for mild Steel in presence of PNMANI-Histidine

Impedance measurements: Figure 6 is the impedance spectra of mild steel with and without the addition of various concentrations of histidine on PNMANI in $0.5MH_2SO_4$. The slightly depressed nature of the semicircle has been attributed to the roughness and inhomogeneities of the solid electrode[34-35]. From Nyquist plot, polarization resistance R_p, charge transfer resistance R_{ct} and are obtained and depicted in Table 6. The R_p and R_{ct} value increases with increasing inhibitor concentration which indicates that the adsorption takes place at the metal surface forming a protective layer. The change in R_{ct} value clearly suggests that charge transfer process controls the dissolution of mild steel.

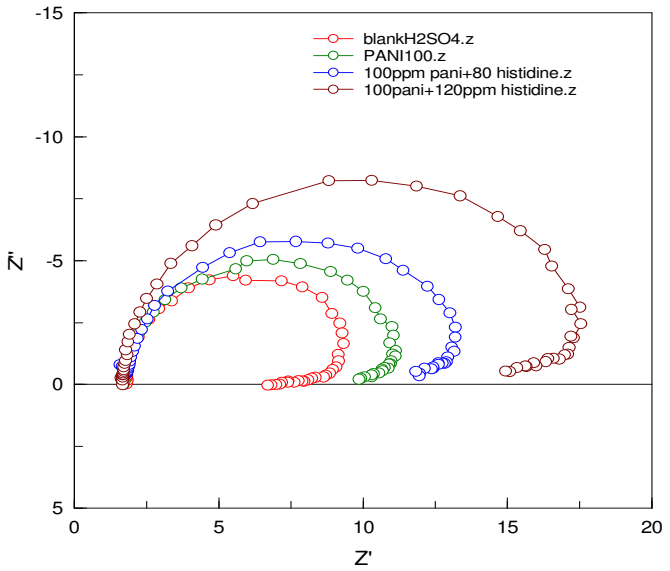

Figure-6
Nyquist plots of mild steel in the presence of PNMANI-Histidine

Table-5
Polarization Parameters PNMANI- Histidine

Conc. (Ppm)	b_a (mV/dec)	b_c (mV/dec)	I_{corr} (µA/cm²)	E_{corr} (V/dec)	IE (%)
Blank	268.6	163.48	5.566	-0.48045	-
100ppm PNMANI	288.6	151.36	2.31	-0.46323	58.67
100ppm PNMANI + 40ppm histidine	214.08	123.63	3.3521	-0.47006	39.77
100ppm PNMANI +80ppm histidine	191.24	115.03	3.0446	-0.45537	45.30
100ppmPNMANI +100ppm histidine	119.92	84.207	1.0672	-0.46291	80.82

Table-6
Impedance parameters in the presence of PNMANI-Histidine

Conc. (Ppm)	R_p (Ohm /cm²)	IE (%)	R_{ct} (Ohm/cm²)	IE (%)
Blank	7.743	-	6.5895	-
100ppm PNMANI	19.29	59.86	9.945	33.71
100ppm PNMANI+ 40ppm histidine	19.99	61.27	10.84	39.25
100ppm PNMANI +80ppm histidine	28.15	72.49	14.77	55.40
100ppm PNMANI 100ppm histidine	31.21	75.19	17.23	61.75

Mechanism of inhibition: The inhibition of PNMANI-histidine on mild steel corrosion in 0.5M H_2SO_4 can be explained by adsorption of inhibitor molecules on metal surface. Initially sulphate ions are adsorbed on the metal surface in H_2SO_4medium. PNMANI which exist as protonated species in acidic solution may interact with already adsorbed sulphate ions on the iron surface. The adsorption may also due to the interaction between unshared electron pairs of nitrogen atom on PNMANI and vacant d-orbitals of the iron atom on the metal surface. The enhanced inhibition efficiency is obtained by synergistic effect of histidine. Due to smaller size and zwitterionic nature of the histidine, they can easily get adsorbed on the mild steel surface. Thus histidine inhibits metal from corrosion and enhances the corrosion protecting efficiency of PNMANI.

Conclusion

PNMANI-histidine showed effective inhibition against mild steel corrosion in 0.5M H_2SO_4. The presence of histidine enhanced the inhibition efficiency of PNMANI and found to be synergistic in nature. The inhibitor system obeyed the adsorption model, Langmuir isotherm. The calculated values of ΔG_{ads}, ΔH_{ads}, ΔS_{ads} indicated the spontenity of the adsorption and its physical nature. Electrochemical measurements showed that PNMANI-histidine acted as a mixed type inhibitor. Also, the higher values of E_a indicated high inhibition efficiency.

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