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Corrosion Inhibition of Mild Steel by Water Soluble Poly (Vinyl Pyrrolidone – Aniline) in 1M HCl

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Abstract

The present work reports the chemical oxidative synthesis of Polyaniline (PANI) in stable aqueous solution/dispersion form, using poly vinyl pyrrolidone (PVP) as an efficient steric stabilizer. This Poly (VinylPyrrolidone - aniline) water soluble composite used as corrosion inhibitor for mild steel in 1M HCl at different concentrations. Weight loss, potenziodynamic polarization and electrochemical impedance spectroscopy measurements were employed. Impedance studies indicated an increase in charge transfer resistance and decrease in double layer capacitance with increase in inhibitor concentration. Potenziodynamic polarization study implies that the inhibitor acts as mixed type inhibitor. Maximum inhibition efficiency was witnessed with 0.2 % percentage of PVPA. The adsorption of the compounds on mild steel surface was found to obey Langmuir's and Temkin's adsorption isotherm. The values of activation energy, free energy of adsorption, heat of adsorption, enthalpy of activation, entropy of activation were also calculated to elaborate the mechanism of corrosion inhibition.

Keywords: Mild steel, Inhibition efficiency, Adsorption isotherm, corrosion inhibitor

Introduction

Conducting polymers had been the topic of the large number of investigations during last decades. Their unique properties such as mechanical strength, electrical conductivity, corrosion stability and possibility of both chemical and electrochemical synthesis make them useful in wide area of applications; such as rechargeable batteries, electro chronic displays, electrochemical sensors, capacitors, and in the last ten years in active corrosion protection.[1-2] Due to ease of synthesis and processing, environmental stability and low synthetic cost, polyaniline is probably the most important industrial conducting polymer today. The use of conducting polymers for the protection of metals against corrosion has been reported. [3-4]

The great potentiality of PANI however, still remains unexploited by its serious problems of insolubility in common organic solvents, non - processability, alteration in structural and electrical properties on ageing etc. To circumvent these problems, one common approach is to prepare PANI composite and blends. In this way PANI based composites, using different water soluble and insoluble support polymers viz. Polyacrylamide (PAAm) [5], Poly vinyl pyrrolidone [6], Methyl cellulose [7], hydrogen ethyl cellulose [8] etc. have been successfully synthesized in stable aqueous/ non aqueous solutions/dispersions.

In this context, the water soluble polymer, Poly vinyl pyrrolidone (PVP) deserves a special mention. This polymer has been reported to be effective for dispersion polymerization of pyrrole [9] and aniline in aqueous acidic condition. It acts as steric stabilizer and it prevents the precipitation of polymerized aniline particles and makes PANI finely dispersed in solution.

The aim of this work is to synthesize water soluble Poly (Vinyl Pyrrolidone - Aniline) PVPA in oxalic acid medium and examine the protection performance of this inhibitor for corrosion of MS in 1M HCl solution. There is no report in literature dealing with inhibition performance of PVPA for corrosion of MS in HCl. The examination of PVPA composite opens up the possibility of conducting polymers having improved properties.

Experimental

Chemicals

Ammonium persulphate, Oxalic acid, aniline and Polyvinylpyrrolidone (M_w=4,000) were purchased from merck chemicals. Aniline was distilled prior to use. All other materials were used without further purification.

Polyvinylpyrrolidone

PVP being a water soluble polymer has a greater affinity towards water. [10] and it has advantageous effects on PANI. It improves polymerization yield, solubility and processability. Polyaniline of high stability and good processibility was prepared in acidic aqueous dispersion / solution using the support of water soluble polymer PVP.

Polymer Preparation

PVPA was prepared by conventional chemical oxidative polymerization method using an oxidant. [11,12] Purified aniline was added to aqueous PVP solution (10%) and the solution was cooled to 2^0 to 5^0C (Solution A).50 ml of 1% $(NH_4)_2S_2O_8$ dissolved in oxalic acid, was added drop wise with constant stirring to solution (A) for a period of one hour. 1:1 mole ratio of aniline to $(NH_4)_2S_2O_8$ was maintained. Polymerization of aniline was allowed to proceed at 2^0 to 5^0C for 3 hrs in thermo stated bath, with occasional stirring. The green coloured emeraldine salt in the form of stable aqueous dispersion was readily obtained. This was treated with ammonium hydroxide for deprotanation. It was isolated from the medium by precipitation technique using non solvent and dried under vaccum.

Material Preparation

Mild steel specimens of size 5cm x 1 cm are used for immersion studies and were lacquered so as to expose area of $1cm^2$ for all electrochemical studies. Before each experiment the specimens were mechanically polished, degreased in absolute ethanol, dried in acetone and stored in a moisture free desiccator.

Weight Loss Method

Pre weighed mild steel specimens(in triplicate) were suspended for different immersion periods, at different temperatures in 1 M HCl without and with inhibitor in various concentrations ranging from 100 to 2000 ppm. After the specified time the coupons were removed from test solution, thoroughly washed, dried well and then weighed. The inhibition efficiency (%) of various concentrations of inhibitor were determined as

$$IE (\%) = W_b - W_I / W_b \times 100 \qquad (1)$$

Where W_b and W_I are the weight loss of mild steel of coupons in the corrodent (blank) and corrodent inhibitor system.

Electrochemical Techniques

Electrochemical studies were carried out in the absence and presence of inhibitor using conventional three electrode cell with larger area platinum foil as counter electrode, MS as working electrode and saturated calomel electrode (SCE) as reference electrode. Solatron Electrochemical analyzer model (1280B) interfaced with an IBM computer and Z plot and Corrware softwares were used for data acquisition and analysis

Results and Discussion

Effect of concentration

Fig.1.implies that increase in inhibitor concentration with time increases the inhibiton efficiency.Maximum efficiency of 93.25 % was accomplished with 0.2 % (2000 ppm) inhibitor concentration at 12 hrs of immersion.This reveals a strong protective layer formation on the surface of mild steel at this immersion time. It is also evident from fig.1 that inhibition efficiency decreases (92.30%) with the increase in the immersion time from 12 to 24 hrs indicating the instability of inhibitor film on the metal surface up to 24 hrs. [13]

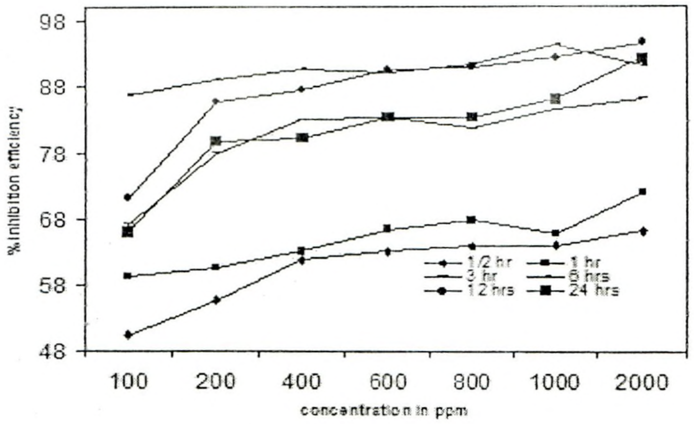

Figure 1: Inhibition efficiency at various concentration of inhibitor and at various immersion times.

Influence of Temperature

Temperature studies were carried out with and without inhibitor of varying concentration at different temperatures ranged from 303 K to 343 K. The results shown in Table.1 indicate that inhibition efficiency increases with temperature upto 333 k. Further increase in temperature illustrates a decrease in efficiency. This findings indicate that at higher temperature the inhibitor molecules are gradually desorbed from the surface of mild steel. [14]

Table 1: Influence of temperature on inhibition efficiency of PVPA on mild steel in 1.0 M HCl.

S.NO	Concentration in ppm	303 K		313 K		323K		333K		343K	
		CR	IE (%)	CR	IE (%)	CR	IE (%	CR	IE (%)	CR	IE (%)
1	Blank	889.63	50.3	629.65	72.15	4999.39	71.34	10,034	72.8	14,917	69.12
2	100	442.19	55.64	732.18	83.15	1433.01	76.47	2730.66	65.44	4606.04	60.37
3	200	394.64	61.76	442.99	85.8	1176.58	82.12	3467.83	84.53	4296.12	75.35
4	400	340.19	63.14	373.32	86.03	1787.78	85.17	1552.70	85.31	3677.05	76.72
5	600	327.92	63.93	367.27	86.47	741.41	85.9	1474.0	84.98	3213.13	78.38
6	800	320.89	64.11	424.85	88.3	704.91	86.46	1507.14	91.12	2310.65	82.62
7	1000	319.29	66.18	342.82	91.84	676.92	91.65	890.99	92.5	2471.75	88.43
8	2000	300.87		214.53		418.45		791.66		1655.79	

Adsorption Isotherm

Adsorption isotherms are very important in determining the mechanism of organo electrochemical reaction. [15] The most frequently used isotherms are Langmuir, Frumkin, Temkin, Fereundlich etc.

Attempts have been made to understand the nature of interaction between the inhibitor and the metal surface in terms of adsorption isotherms. [16,17] In this study surface coverage values revealed that the isotherms that best describe the adsorption characteristics of PVPA composite on mild steel surface are Langmuir and Temkin adsorption isotherms.

Temkin adsorption isotherm is given by the equation,

$$\theta = k \ln C \tag{2}$$

Here, θ is the surface coverage, C is the concentration of the inhibitor solution and k is an adsorption coefficient. A Plot of log C versus θ should give a straight line with unit slope. When θ is smaller, the interaction among adsorbed molecules can be neglected, and the behaviour of adsorption is affected by the heterogeneity of electrode surface. Temkin isotherm is applicable to this case. It was found that the extent of adsorption of the inhibitor is increased with the concentration. This behaviour could be attributed to the increasing surface coverage (θ) with adsorption of the inhibitor molecules at high concentration.

The Langmuir isotherm can be represented by following equation,

$$C / \theta = 1 / k + C \tag{3}$$

Plots of log (C/θ) Vs log C were linear confirming that the Langmuir adsorption isotherm (Fig.2) is valid for the adsorption of inhibitor on mild steel, proving that there is no interaction between the adsorbed species.

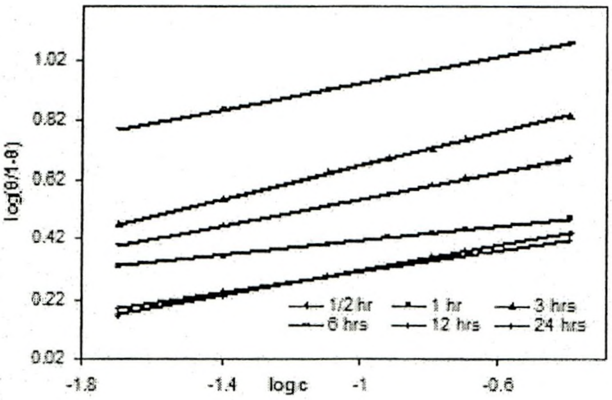

Figure 2: Langmuir isotherm model for adsorption of PVPA on mild steel in 1M HC1.

Arrhenius plot & Activation Energy

To comprehend the effect of temperature on the corrosion process in the presence of the inhibitor, the Arrhenius equation is helpful.

$$\text{Log CR} = \frac{-E_a}{2.303\ RT} + \log A \tag{4}$$

Where CR is the corrosion rate, E_a is the apparent activation energy, R is the molar gas constant, T is the absolute temperature, and A is the frequency factor. Arrhenius plot of log CR vs. 1/T for mild steel in the absence and presence of various concentration of PVPA gives E_a values. These values were obtained from the slope of this plot. The energy of activation decreased in the presence of inhibitor. Table.2. reveals that E_a value is slightly higher at the lower concentration of inhibitor and decreases with increased inhibitor concentration. The lower values of activation energy at higher concentration of the inhibitor is explained as the specific interaction between metal and the inhibitor molecule.

Table 2: Kinetic and Thermodynamic Parameters of MS in the presence of PVPA.

Concentration of the inhibitor in ppm	Activation Energy E_a KJ/mole	Free Energy of Adsorption - ΔG = KJ/mole					Change in enthalpy ΔH J/mole	Change in Entropy ΔS J/mole
		303 K	313 K	323 K	333 K	343 K		
100	22.00585	34.3405	35.918	37.4955	39.073	40.6504	-13457.09	157.75
200	12.06348	33.4942	34.7899	36.0856	37.3813	38.677	-5287.57	821.38
400	16.49893	32.7349	34.0427	35.3505	36.6582	37.966	-1070.676	1009.298
600	16.52162	31.9035	33.2291	34.5548	35.8804	37.206	-1278.853	1013.668
800	16.44059	29.5038	32.6081	33.9424	35.2767	36.6111	-838.765	1006.552
1000	18.36887	28.8973	32.3728	33.8666	35.3605	36.8543	-4134.065	1119.563
2000	18.14314	25.032	30.3503	32.434	34.5176	36.6013	-14803.76	1394.817

Thermodynamic and kinetic parameters

The equilibrium constant of adsorption k is related to the free energy of adsorption according to equation (5)

$$\Delta G_{ads} = -2.303\ RT\log\ (55.5\ K) \qquad (5)$$

The values of K calculated from Arrhenius equation were used to compute the values of free energy. The negative sign of the free energy of adsorption ΔG^0 (Table 2) indicates that the adsorption of inhibitor at the metal surface is a spontaneous process. [18] This suggests that the inhibitors are strongly adsorbed on mild steel surface. Generally, values of ΔG^0_{ads} up to -20 $kJmol^{-1}$ are consistent with electrostatic interaction between charged molecules and a charged metal which indicates physical adsorption, while the values more negative than this involve charge sharing or transfer from the inhibitor molecules to the metal surface to form chemical adsorption.[19-20] The negative values of ΔH obtained indicate that the adsorption process is spontaneous, while the positive sign of ΔS shows a decrease in the system disorder [21].

Linear Polarization Method

PVPA reduces the corrosion current density I_{corr} and the suppression in current increases with increasing concentration of inhibitor. The presence of PVPA does not remarkably shift the corrosion potential E_{corr} and hence can be said to be a mixed type inhibitor in1.0 M HCl. Tafel slope values b_a & b_c were not affected significantly in inhibited solution as compared to uninhibited solution. This observation suggests that inhibitor molecules adsorb on the metal surface by blocking the active sites on the metal surface. [22] The polarization resistance (R_P) values of mild steel in 1 M HCl in the presence and absence of different concentrations of the inhibitor are given in Table.3. The percentage inhibition Efficiency (%IE_{Rp}) is calculated as follows

$$\% \, IE_{Rp} = 100 \, (1 - R_P / R'_P) \qquad (6)$$

Where R_P and R_P' are the polarization resistance with and without inhibitor respectively. R_P (Fig.3) increases with increasing the inhibitor concentration and IE was found to be 85.66 % using R_P values at 2000 ppm concentration. In agreement to the weight loss results, the inhibition efficiency of polarization studies increases with inhibitor concentration.

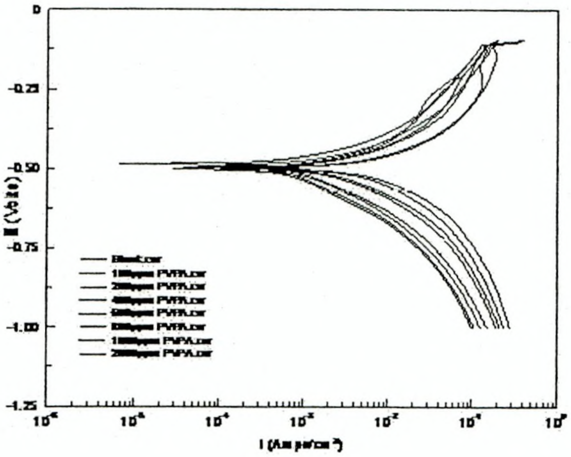

Figure 3: Polarization curves for mild steel at various concentrations of PVPA in 1M HCl.

Table3. Polarization data of MS in the presence of PVPA

Conc. of the inhibitor in ppm	E_{corr} Mv / sec	i_{corr} (mA /cm^2 x 10^{-4})	b_a mV / dec	b_c mV / dec	IE %	R_p Ohm / cm^2	IE %
Control	-497	58.32	186	160		4.47	
100	-498	47.26	195	145	18.97	5.52	18.97
200	-496	25.28	145	124	56.64	10.32	56.65
400	-499	22.15	156	128	62.02	11.78	62.0
600	-492	13.84	184	106	76.27	18.85	76.27
800	-503	15.44	248	140	73.53	16.9	73.53
1000	-502	11.33	204	106	80.58	23.03	80.58
2000	-487	8.36	185	99	85.66	31.20	85.66

Impedance Measurements

The parameters derived from the Nyquist plot (Fig.4) in presence and absence of inhibitor are shown in Table 4. The charge transfer resistance (Rct) increases with increase in inhibitor concentration. As the PVPA concentration increases, the R_{ct} values increase but $C_{dl\ values}$ tend to decrease. The decrease in C_{dl} values is due to the adsorption of PVPA on the surface of metal which reduces the metal surface area undergoing corrosion. It has been reported that the adsorption process on the metal surface is characterized by a decrease in $C_{dl.}$ [23] The adsorption of PVPA on the metal surface can occur directly on the basis of donor -acceptor interactions between π electrons of polymer chain and the vacant d-orbitals of iron surface atoms or an interaction of PVPA with already adsorbed chloride ions as proposed by Hackerman etal. [24]

Table 4: Electrochemical data for the corrosion of Mild Steel in 1M HCl.

Concentration of the inhibitor in ppm	$R_{Ct\ Ohm/cm^2}$	IE %	Cdl µF / cm^2	θ
Control	24.47		43.32	
100	34.41	28.88	26.96	0.38
200	43.51	43.77	17.59	0.59
400	73.87	66.87	14.38	0.67
600	92.05	73.42	9.8	0.77
800	118.53	79.36	10.23	0.76
1000	166.33	85.29	10.18	0.77
2000	175.58	86.06	9.67	0.78

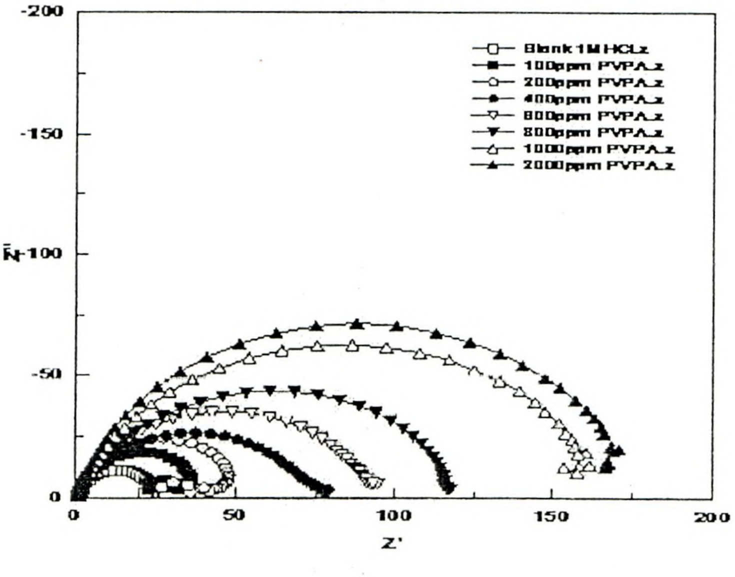

Figure 4: Nyquist plots for mild steel at different concentrations of PVPA in 1M HCl.

Efficient Inhibitor PVPA

In this study, maximum I.E. 93.25% was obtained with 0.2 % concentration of water soluble inhibitor. The corrosion inhibition efficiency of PVPA is much larger at lower concentration than quaternary ammonium salts and monomer aniline. Percentage inhibition efficiency of aniline monomer at 20,000 ppm was 54% [25] comparatively much less than 0.2 % of Poly (VinylPyrrolidone - Aniline) composite reported in this study. Higher inhibition efficiency in the state of PANI was reported [26] which is due to greater availability of π e^{-}s in the aromatic ring whose orientation on metal surface is usually coplanar. But it does not have stability on storage. But the solution of PVP stabilized PANI showed an excellent storage stability and good inhibition efficiency.

Conclusion

Poly (VinylPyrrolidone -Aniline) water soluble composite acts a good inhibitor for corrosion of mild steel in 1.0 M HCl. The inhibition efficiency increased with increase in PVPA concentration and significantly affected by the temperature rise. The inhibitor obeys Langmuir and Temkin adsorption isotherm. The values of ΔG^0_{ads} are negative, which implies that the inhibitors were strongly adsorbed on the mild steel surface. Kinetic and thermodynamic parameters infer the strong adsorption of inhibitor molecules on MS surface and also the inhibition is by spontaneous chemical adsorption. Potenziodynamic polarization curves reveal the mixed mode of inhibition. The results obtained from weight loss, impedance and polarization studies are in good agreement.

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