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ORIGINAL ARTICLE

Poly (vinyl alcohol – aniline) water soluble composite as corrosion inhibitor for mild steel in 1 M HCl

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Abstract Poly (vinyl alcohol – aniline) PVAA composite was tested for its performance in protecting mild steel MS against corrosion in 1 M HCl. The inhibitive parameters were evaluated by means of weight loss, electrochemical polarization and impedance methods. Results indicated that the addition of PVAA to the acid reduces the corrosion of the metal. Inhibition efficiency increases with increase in inhibitor concentration. The results further revealed that PVAA at a concentration of 2000 ppm furnishes a maximum of 92% inhibition efficiency. Thermodynamic parameters such as free energy of adsorption, heat of adsorption, etc., had been evaluated from temperature studies. The adsorption of PVAA followed Langmuir and Temkin adsorption isotherms. Polarization curves revealed that PVAA is a mixed inhibitor.

1. Introduction

Corrosion is an electrochemical phenomenon and is accompanied by the flow of electrical current. One can minimize the rate and quantum of corrosion only by providing a suitable environment in which current cannot flow at interfaces. The best corrosion protection is to build a barrier separating the metal from its environment. Protection of mild steel MS from corrosion is a matter of practical importance. Acids are widely used in industries such as pickling, cleaning, descaling, etc. Because of the aggressiveness of the acids, inhibitors are used to reduce the rate of dissolution of metals. The most effective and efficient inhibitors are organic compounds having π electrons in their structure. Conducting polymers are conjugated systems having alternate single and double bonds and therefore rich in π electrons, hence effectively reduces metallic corrosion. Therefore, conducting polymers due to their inherent polar nature should offer better corrosion inhibition efficiencies than simple organic compounds. The earlier studies (Grchev et al., 1991; Manivel and Venkatachari, 2007, 2004, 2006; Sathiyanarayanan et al., 1992; Siddaraman, 2005; Schorr and Yahalom, 1972) have shown that inhibitive properties of polyaniline and its derivatives on the corrosion of iron in acid solution are due

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to the presence of π electrons, quaternary nitrogen atom and the large molecular size of them. In this study the inhibitive behaviour of poly (vinyl alcohol – aniline) PVAA on MS in 1 M HCl solution has been studied.

2. Experimental

2.1. Reagents used

Ammonium persulphate, oxalic acid, aniline and polyvinyl alcohol (M_w = 12,000) were purchased from Merck Chemicals. Aniline was distilled prior to use. All the other chemicals were used without further purification.

2.2. Polymer preparation

The method used to prepare PVAA composite was adopted from the procedure described by Gangopadhyay et al. (2001) and Mirmohseni and Wallace (2003). 1% aniline was well mixed with 10 % PVA solution by constant stirring. To this solution 20 ml of equimolar mixer of ammonium persulphate and aniline in 1 M oxalic acid was added below 5 °C. Polymerization was allowed to proceed for 3 h and the composite formed as a bright green stable solution. It was deprotanated and the pH of the solution was maintained around 9 by adding drops of 1 M NH_4OH which was allowed to stay for 5 h. PVAA composite was isolated from the medium by precipitation technique using a non solvent and dried under vacuum.

2.3. Weight loss method

MS specimens were cut in to 5 × 1 cm coupons for immersion studies and were lacquered so as to expose an area of 1 cm^2 only for all electrochemical studies. The specimens were mechanically polished, their edges were abraded with fine grade emery paper, degreased and dried in acetone, stored in a dessicator and used for all studies. Weight loss measurements were carried out in triplicate in the absence and presence of various concentrations of PVAA in 1 M HCl for various periods of immersion at different temperatures including room temperature. From the data, corrosion rate and inhibitor efficiency were calculated.

2.4. Electrochemical measurements

Electrochemical studies were carried out in the absence and presence of an inhibitor using conventional three electrode cell with a platinum foil having a larger surface area as a counter electrode, MS plate as a working electrode and a saturated calomel electrode as the 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.

3. Results and discussion

It is normally expected that compounds with high molecular weight and bulky structure may cover more area on the active electrode surface. If such a bulky molecule can have a chemisorptive property it is naturally expected to inhibit corrosion more effectively.

3.1. Weight loss method

3.1.1. Effect of concentration

Corrosion rate of the metal and inhibitor efficiency of the polymer obtained by weight loss method for different inhibitor concentrations at various periods of immersion in 1 M HCl are provided in Table 1. IE of the inhibitor increases with an increase in inhibitor concentration. Maximum efficiency of 90.01% has been achieved with 2000 ppm for an immersion period of 12 h. The increase in inhibition efficiency with an increase in the concentration of the inhibitor can be explained on the basis of increased adsorption of the composite on the metal surface which gets manifested as the increasing trend in the surface coverage with concentration (Ashassi-Sorkhabi et al., 2005).

3.1.2. Effect of immersion time

For any concentration of the inhibitor studied maximum efficiency was recorded for 12 h of immersion which also shows that for all concentrations, IE increased with immersion time. This increase of IE with respect to the time of immersion indicates the stability and persistence of the inhibitor films on the metal surface (Mohammed Ajml et al., 2000). The decrease in

Table 1 Corrosion rate and inhibition efficiency data obtained from weight loss measurements in 1.0 M HCl in absence and presence of PVAA composite.

Concentration of the inhibitor in ppm	Immersion time (h)											
	0.5		1		3		6		12		24	
	CR mpy	I.E (%)	CR mpy	I.E (%)	CR mpy	I.E (%)	CR mpy	I.E (%)	CR mpy	I.E(%)	CR mpy	I.E(%)
Blank	1820.2		1607.4		1593.9		1448.8		714.36		1374.9	
100	856.49	52.95	630.82	60.76	738.86	63.00	939.83	35.94	504.20	29.32	717.85	47.79
200	726.98	60.06	525.71	67.3	636.33	72.00	817.98	43.55	477.38	33.17	659.4	52.04
400	690.34	62.07	484.07	69.89	399.02	75.00	610.30	57.88	450.0	41.88	631.67	54.05
600	624.49	65.69	433.05	73.06	336.52	78.89	524.35	63.81	370.32	61.86	547.24	60.21
800	594.83	67.32	402.0	74.98	318.06	80.05	424.16	70.73	224.05	68.64	449.05	67.68
1000	548.61	69.55	386.0	76.00	315.22	80.22	249.4	82.79	109.63	84.7	389.23	71.69
2000	469.68	74.61	315.08	80.4	216.35	86.43	186.46	87.13	72.00	90.01	228.76	83.36

CR – corrosion rate and I.E – inhibition efficiency.

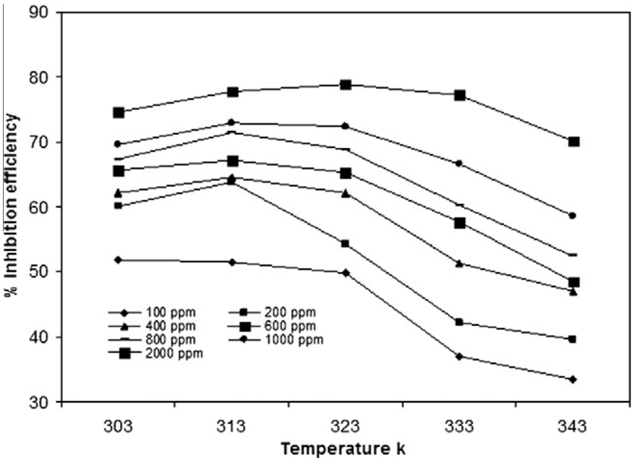

Figure 1 Variation of inhibition efficiency with temperature.

inhibition efficiency after 24 h of immersion may be due to the desorption of adsorbed layer.

3.1.3. *Effect of temperature*

The effect of temperature on the inhibition efficiency in 1 M HCl containing various concentrations of inhibitor at temperatures ranging from 303 K to 343 K are depicted in Fig. 1. Inhibition efficiency increases up to 323 K, a further rise in temperature showed the decrease in efficiency indicating that the adsorption phenomenon predominates over desorption up to 323 K where as the reverse comes into effect at 333 K and thereafter. Zacchini et al. (1971) has attributed the decrease of inhibition efficiency with a rise in temperature to the alteration of the rate of adsorption/desorption ratio. Hence in the present study the rate of desorption of PVAA should be faster than the rate of adsorption at higher temperatures bringing down the inhibition efficiency.

3.1.4. *Adsorption isotherm*

It is generally accepted that the organic molecules inhibit corrosion by getting adsorbed at the metal/solution interface and that the degree of adsorption depends on their chemical structure, chemical composition of the solution, the nature of metal surface, the temperature and the electrochemical potential at the metal/solution interface (Riggs, 1973).

The nature of inhibitor interaction on the corroding surface during corrosion inhibition of the metal has been deduced in terms of adsorption characteristics of the inhibitor. The surface coverage (θ) values are very useful while discussing the adsorption characteristics. The surface coverage of the inhibitor at a given concentration is calculated by using the equation,

$$\theta = \mathrm{IE}/100 \tag{1}$$

Attempts have been made to fit θ values to the thermodynamic – kinetic model of El. Awady et al., Freundlich, Temkin and Langmuir isotherms.

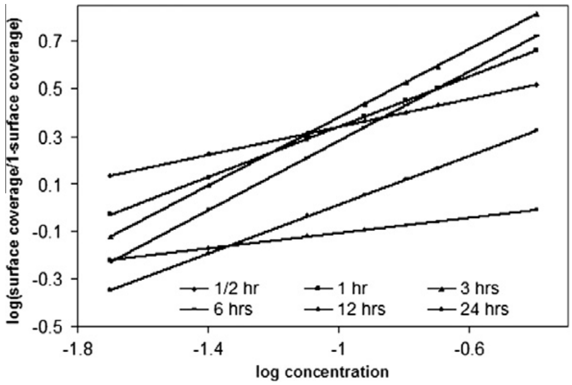

Figure 2 Langmuir's adsorption plots of PVAA composite in 1.0 M HCl.

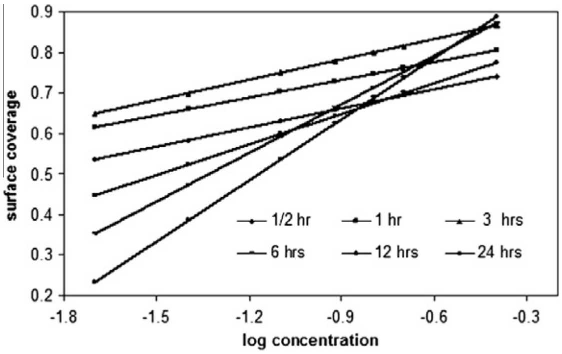

Figure 3 Temkin's adsorption plots of PVAA composite in 1.0 M HCl.

A plot of log ($\theta/1 - \theta$) vs log c was a straight line as seen in Fig. 2 indicating that the adsorption of tested inhibitor in 1 M HCl solutions on the MS surface obeys Langmuir adsorption isotherm (Bouklah et al., 2005). A plot of the logarithmic concentration of the inhibitor with surface coverage shows a linear relationship as observed in Fig. 3 confirming the applicability of Temkin adsorption isotherm also (Damaskin et al., 1971). This indicates that the process of inhibition is mainly by adsorption of PVAA on MS surface.

3.1.5. *Energy of activation E_a and thermodynamic parameters*

The dependence of logarithmic corrosion rate on the reciprocal values of the absolute temperature is seen as straight lines. The values of the slope of these straight lines permit the calculation of activation energy Ea by the application of the equation,

$$\mathrm{CR} = Ae^{(-\mathrm{Ea}/RT)} \tag{2}$$

where A is the frequency factor for the reaction, R is the universal gas constant, T is the temperature (K). Decrease in energy of activation in the presence of an inhibitor is observed as seen in Table 2. This is explained by (Putilova Bishop, 1960) that in presence of chemisorbed inhibitor at high degree of coverage, the rate determining step in the dissolution of the metal becomes the diffusion process through the layer formed by adsorbed inhibitor and corrosion products. Similar results are reported by Ibrahim et al. (1987) during their study of the mechanism of the inhibition of 3, 5-diaminobenzoic acid towards the corrosion of MS in 1 M HCl. This also suggests that such inhibitors are firmly held on the metal surface (Putilova et al., 1960; Debri and Ozean, 2006). Change in free energy (ΔG) of adsorption of the inhibitor was obtained by applying the following equation

Table 2 Kinetic and thermodynamic parameters calculated from weight loss measurements for mild steel in 1.0 M HCl.

Concentration of the inhibitor in ppm	Activation energy E_a (kJ/mole)	Free energy of adsorption – ΔG_{ads} = 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	22.52	33.87	34.38	34.89	35.40	35.91	−18442.8	50.91
200	20.24	33.06	33.44	33.82	34.20	34.59	−7604.29	751.47
400	18.02	31.66	32.11	32.56	33.01	33.47	−7326.04	1179.39
600	19.29	31.03	31.46	31.87	32.29	32.70	−1606.08	929.98
800	19.17	29.88	31.03	31.47	31.90	32.34	−1635.204	1038.82
1000	18.27	29.50	30.84	31.35	31.85	32.36	−5187.61	1160.94
2000	17.40	29.06	30.84	28.02	30.96	33.89	−15377.4	5799.88

$$\mathrm{LogC} = [\log \theta/1 - \theta] - \mathrm{LogB} \quad (3)$$

$$\mathrm{LogB} = -1.74 - (\Delta G/2.303RT) \quad (4)$$

where C is the concentration of the inhibitor, θ is the surface coverage, T is the temperature and R is the gas constant. The negative values of ΔG obtained indicates the spontaneity of the adsorption process and stability of the adsorbed layer on the MS surface.Change in free energy values of adsorption (ΔG_{ads}) at different temperatures were used to calculate ΔS and ΔH from Gibbs Helmholtz equation.

$$\Delta G = \Delta H - T\Delta S \quad (5)$$

where ΔS is entropy of adsorption and ΔH is enthalpy of adsorption. The negative values of ΔG and ΔH and the positive values of ΔS provided in Table 2 are characteristics of strong interaction between the inhibitors and the metal surface forming a protective layer on the MS surface (Bag et al., 1996). The negative value of ΔH indicates that the adsorption of inhibitor molecules on the metal surface is an exothermic process. Positive values of ΔS shows a decrease in the system disorder (El and Etre, 2006).

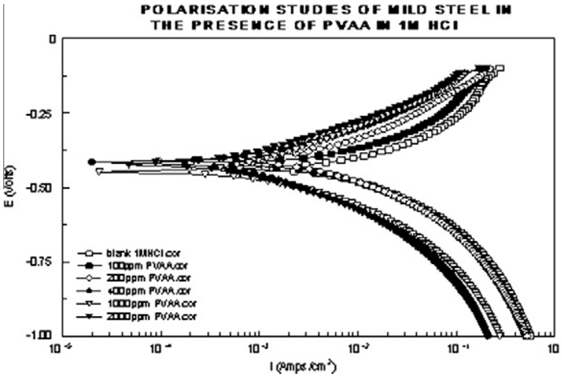

Figure 4 Potenziodynamic polarization curves of mild steel in 1.0 M HCl.

3.2. Potentiodynamic polarization studies

The potentiodynamic polarization curves of MS in 1 M HCl with the addition of various concentrations of PVAA are shown in Fig. 4. The corrosion kinetic parameters such as corrosion current density i_{corr}, corrosion potential $E_{corr,}$ anodic Tafel slope b_a and cathodic Tafel slope b_c deduced from the curves are given in Table 3. The corrosion current density values decrease from 60.84 $\mathrm{mA/cm^2} \times 10^{-4}$ for the blank acid to 5.08 $\mathrm{mA/cm^2} \times 10^{-4}$ for the addition of 2000 ppm PVAA resulting in 91.63% of inhibition efficiency. As in the case of weight loss method, the increase in concentration of the inhibitor decreases the i_{corr} values. $E_{corr,}$ b_a and b_c values do not change appreciably with the addition of the inhibitor indicating that the inhibitor is not interfering with the anodic dissolution or cathodic hydrogen evolution reactions independently but acts as a mixed type of inhibitor (Sathiyanarayanan et al., 2005; Jayaprabha et al., 2005). Polarization resistance values R_P obtained from the LPR method show a steep increase of R_P from 4.29 Ω/cm^2 for that of the blank to 53.68 Ω/cm^2 for the addition of the highest concentration of inhibitor. The increase of R_P values with concentration of PVAA too indicates its effective inhibitive action.

3.3. Electrochemical impedance studies

Electrochemical impedance values of MS in 1 M HCl in the absence and presence of various concentrations of PVAA are depicted in Fig. 5. These plots having the shape of a semicircle for all the concentrations of PVAA examined indicate that the corrosion is mainly controlled by charge transfer process. The charge transfer resistance R_{ct} and the interfacial double layer

Table 3 Electrochemical kinetic parameters in the presence and absence of inhibitor.

Concentration of the inhibitor in ppm	E_{corr} (mV/sec)	i_{corr} ($\mathrm{mA/cm^2} \times 10^{-4}$)	b_a (mV/dec)	b_c (mV/dec)	IE (%) using i_{corr}	R_p (Ω/cm^2)	IE (%) using R_P
Blank	−437	60.85	124	98		4.29	
100	−421	37.92	126	100	37.68	6.88	37.67
200	−408	26.90	72	67	55.79	9.70	55.78
800	−416	7.11	108	84	88.31	36.68	88.31
1000	−447	6.73	61	63	88.96	38.79	88.94
2000	−422	5.09	92	80	91.63	53.68	92.00

i_{Corr} = corrosion current density, E_{Corr} = corrosion potential, b_a and b_c = Tafel constants, and R_p = Polarization resistance.

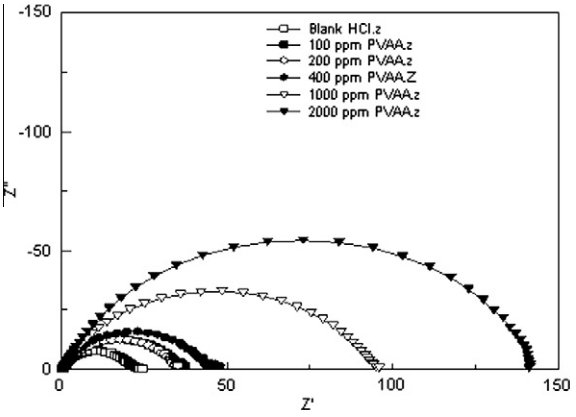

Figure 5 Nyquist plots of mild steel in 1.0 M HCl.

Table 4 Electrochemical kinetic parameters obtained by impedance technique in 1.0 M HCl in the absence and presence of different concentrations of PVAA composite.

Concentration of the inhibitor in ppm	R_{Ct} (Ω/cm^2)	IE %	C_{dl} (μF/cm^2)	θ
Blank	21.23		35.06	
100	34.83	39.05	32.70	0.067
200	34.33	38.16	30.35	0.134
800	42.83	50.43	26.93	0.232
1000	92.88	77.14	15.32	0.563
2000	142.21	85.07	13.31	0.62

C_{dl} = double layer capacitance and θ = surface coverage.

capacitance C_{dl} derived from these curves are given in Table 4. R_{ct} increases from the value of 21.23 Ω/cm^2 for the blank to 142.21 Ω/cm^2 for the highest concentration of PVAA providing 85.07% inhibition efficiency. Thus increase in R_{ct} with an increase in the concentration of PVAA indicates the adsorption of inhibitors on the metal surface (Yurt et al., 2004). C_{dl} decreases from 35.06 μF/cm^2 for the blank to 13.31 μF/cm^2 for 2000 ppm PVAA. The decrease in the capacitance C_{dl} at the MS solution interface with the increase in inhibitor concentration may be due to the strong adsorption of these composite molecules at the interface, since according to electro chemical theory a decrease in C_{dl} is proportional to the adsorption rate (Lorenz and Mansfeld, 1981). The C_{dl} values are also used to calculate the surface coverage θ using the relationship (Khaled and Hackerman, 2003; Elkadi et al., 2000).

$$\theta = \frac{C_{dl} - C'_{dl}}{C_{dl}} \tag{6}$$

where C_{dl} and C'_{dl} are the double layer capacitance values in the absence and presence of inhibitors.

3.4. Inhibition mechanism

Corrosion inhibition of MS in hydrochloric acid solution by PVAA can be explained on the basis of molecular adsorption. The compound inhibits corrosion by controlling both the anodic and cathodic reactions. In acidic solutions the composite inhibitor exists as a protonated species. These protonated species adsorb on the cathodic sites of the MS and decrease the evolution of hydrogen. The adsorption on anodic sites occurs through π-electrons of aromatic rings and a lone pair of electrons of the nitrogen atom, which decreases the anodic dissolution of MS (Quraishi et al., 2000). The high performance of the polymer is attributed to the presence of π electrons, quaternary nitrogen atom and its larger molecular size.

4. Conclusion

PVAA is found to be a good inhibitor which brings out a maximum of 92% inhibition efficiency of MS corrosion in 1 M HCl. This composite proved to be a better inhibitor than the quaternary ammonium salts, aniline and polyanilne due to the following facts.The inhibitive nature of this composite is much larger at lower concentrations than simple quaternary ammonium salts and aniline. Percentage inhibition efficiency of aniline at 20,000 ppm was reported as 54% (Sathiyanarayanan et al., 1994) which is comparatively much lower than the efficiency of 2000 ppm of PVAA composite as concluded in this study. Higher inhibition efficiency in PANI was reported (Sathiyanarayanan et al., 1992) which is due to greater availability of π electrons in the aromatic ring whose orientation on the metal surface is usually coplanar but it does not have stability on storage. The solution of PVA stabilized PANI having initial concentration of 0.1–0.3% showed excellent storage stability over 6 months. In PVAA composite, the PANI should be a corrosion inhibitor, since increasing the concentration of PANI in the composite increases the corrosion inhibition. But increasing % of PANI in the composite has been restricted because of the lower solubility of the composite in water. Moreover in the solution prepared with higher percentage of aniline, precipitation of free PANI occurred during storage (Gangopadhyay et al., 2001). So, instead of using higher composition of aniline in the composite, higher concentration (2000 ppm) of the composite itself is used to bring about maximum efficiency. Thus PVAA plays a major role in reducing the metal dissolution as well as hydrogen evolution and protecting the MS surface.

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