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An electrochemical study of Polyvinyl Alcohol as corrosion inhibitor of mild steel in sulphuric acid

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ABSTRACT

Corrosion being inevitable can cause deterioration not only in economic but health and safety areas too. The serious consequences of the corrosion process have become a problem of worldwide significance. Therefore, with the advances in technology, it has become guite important to take steps to prevent corrosion. The corrosion inhibition effectiveness of Polyvinyl Alcohol on mild steel in 1 N H₂SO₄ was investigated using electrochemical methods and surface analysis. The electrochemical impedance and potentiostatic calculations were done at various concentrations and temperatures. The data obtained showed that the inhibition efficiency increased with increase in the concentration of Polyvinyl Alcohol and also again showed an increase with increase in the temperature with the highest efficiency being 89.4% at 338K. Tafel polarization studies reveal that it acts as an efficient mixed type inhibitor. The temperature kinetics studies indicate monolayer adsorption of the inhibitor on the mild steel surface. The activation parameters governing adsorption show that the inhibitor is physically adsorbed. FTIR spectroscopy reveals the possible binding sites of polymer during adsorption on metal surface. The surface images recorded from Scanning Electron Microscope and Quantum chemical parameters such as highest occupied molecular orbital energy (E HOMO), lowest unoccupied molecular orbital energy (E LUMO), energy gap (ΔE), dipole moment (µ) etc. have been found to supplement the results obtained from electrochemical measurements.

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INTRODUCTION

Polymers have a wide range of applications that far exceeds that of any other class of material available to man. Because of their high molecular weight, polymers have fascinated corrosion chemists to use them as corrosion inhibitors ⁽¹⁻⁹⁾. In the present study, Polyvinyl Acohol, a polymer's role as a corrosion inhibitor is exhibited. The improved inhibition efficiency is be due to Larger molecular area and weight which allows better absorption of the polymeric film on the surface of the metal. The polymeric chain can displace the water molecules from the metal surface thereby lowering the entropy of the system. Also the polymer has a multiple bonding sites which makes desorption of the polymer a slow process leading to a stronger and effective polymeric film on the surface of absorption and hence show better inhibitive properties.

EXPERIMENTAL PROCEDURE

MILD STEEL (1cm x 1cm) samples were prepared by means of a polishing /emery papers of different grades i.e. 100, 320, 600 and 1000, degreased with acetone, rinsed and sonicated with distilled water prior to immersion in the polarization cell.**Polyvinyl Alcohol** was prepared at three different concentrations (v/v) of 0.5%, 1.0% and 2%.Potentiodynamic Polarisation Studies, Impedance Measurements, Potentiostatic Polarisation Studies, Temperature kinetics studies, Surface Morphology and Quantum Chemical Calculations were used to investigate the inhibition of corrosion in acidic media.

RESULTS

Logarithm of current densities were plotted against corresponding potentials and various parameters, OCP, i_{corr} , β_a and β_c , and I% were calculated which are given in the Table 1.



Figure 1.1: Polyvinyl Alcohol at 308 K



Figure 1.2: Polyvinyl Alcohol at 318 K

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Figure 1.3: Polyvinyl Alcohol at 328 K

Figure 1.4: Polyvinyl Alcohol at 338 K

Table 1 clearly shows that the corrosion currents decrease in presence of inhibitor compared to acid and are lowest for the highest concentration of Polyvinyl alcohol i.e. 0.350 mAcm⁻² for 1% at 338K.The inhibition efficiency increases with increase in the concentration of the inhibitor.

Conc. (mass %)	Temp. (Kelvin)	E _{corr} (-) mV	i _{corr} (mA.cm- ²)	β_{c} (mV/dec)	β _a (mV/dec)	I %
H ₂ SO ₄	308	510	1.000	140	40	
0.25		483	0.546	180	150	45.3
0.5		440	0.439	160	40	56.1
1		500	0.369	165	65	63.1
H_2SO_4	318	520	1.479	130	40	
0.25		470	0.619	110	30	58.1
0.5		450	0.47	115	50	68.2
1		460	0.349	30	20	76.4
H_2SO_4	328	510	2.454	60	20	
0.25		450	0.778	80	50	68.3
0.5		425	0.505	160	50	79.4
1		400	0.427	60	60	82.6
H_2SO_4	338	510	3.311	30	20	
0.25		480	0.834	110	60	74.8
0.5		475	0.543	120	60	83.6
1		485	0.35	130	60	89.4

Table 1Corrosion Parameters of Mild Steel in 1N H₂SO₄ in the presence of Polyvinyl Alcohol

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The efficiency of the inhibitor also increases with the increase of the temperature the inhibition efficiency is highest 89.4% at 338K as compared to 63.1% at 308K for 1% of Polyvinyl Alcohol. Hence the inhibitors belong to the third category of inhibitors as given by Putilova which retards corrosion at elevated temperature efficiently but corrosion is higher at lower temperature. There is no appreciable shift in the OCP values in uninhibited solutions and that of solutions having various concentrations of Polyvinyl Alcohol at all temperatures. This indicates that this inhibitor behaves as mixed type inhibitor and gets equally adsorbed on the cathodic and anodic sites suppressing both the partial electrochemical reactions to an equal extent.

Electrochemical impedance Studies

The impedance parameters for mild steel in 1N H₂SO₄ with and without Polyvinyl alcohol at 308 K are deduced from the analysis of Nyquist and Bode plots are given in Table 2.

Table 2 Impedence Parameters for the Corrosion of Mild steel in 1N H₂SO₄ and in presence of Polyvinyl alcohol

Inhibitor	$R_{ct}(\Omega cm^2)$	f (Hz)	C _{dl} (Fcm ⁻²)	1%
1N H ₂ SO ₄	96.7	5.486	3 × 10 ⁻⁴	
1 % Polyvinyl alcohol	177.3	3.742	2.4 × 10 ⁻⁴	45.4



Figure 2.1Nyquist plot for mild steel at 308KFigure 2.2 Bode plot for of mild steel at 308K

In the presence of inhibitors, the impedance response of mild steel in 1N H_2SO_4 changes significantly. The diameter of the capacitive loop increases in the presence of additive as compared to the acid, which indicates the inhibition of corrosion process. The value of charge transfer resistance (R_{ct}) increases in the presence of additives and this in turn leads to a decrease in i_{corr} for mild steel in the acidic solution. The double layer capacitance is directly related to the dielectric constant of the medium and is inversely related to the double layer thickness. This can also be related to adsorption at the metal /solution surface. In the present case, C_{dl} value decreases on the addition of inhibitor revealing that a complete film is formed on the metal surface when dipped inhibitor solution. The decrease in C_{dl} indicates the adsorption of the inhibitors on the mild steel surface.

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PotentiostaticPolarisation Studies

The steady state potentiostatic behaviour of the anodic dissolution of mild steel in 1N H_2SO_4 in presence of Polyvinyl alcohol was studied. The representative polarization curves are shown in Fig.3.The various passivating parameters (Ic-critical current, Ip-Passivating potential were determined and are given in Table 3.



Figure3 Potentiostatic Polarization curve for the Mild Steel in various concentrations of Polyvinyl alcohol

 Table 3Electrochemical Parameters of Anodic Dissolution of Mild Steel in 1N H₂SO₄

 in presence of different concentrations of Polyvinyl alcohol

				<u> </u>	
Solution	Conc.(%)	E _{pp} (mV) (Passivating Range)	i _c (mAcm ⁻²)	i _p (mAcm⁻ ²)	
H ₂ SO ₄	1 N	590-1050	239.8	9.98	
Polyvinyl Alcohol	0.25%	560-1540	54.6	0.74	
	0.5%	536-1575	0.086	0.01	
	1.0%	560-1560	49.2	0.66	

It is evident from the figure3 that there is significant decrease in the i_c and i_p values in the presence of Polyvinyl alcohol The drop in the i_p and i_c values increases with increase in the concentration of the additive. The stretch of passivation range increases with the increase in the concentration. The passivation range is also largest for 2.0% solution of Polyvinyl alcohol i.e from 480-1360 mV.

Temperature Kinetic Studies

Attempts were made to fit θ values to the Thermodynamic-kinetic model of Temkin and Langmuir isotherms and the correlation coefficient (R²) values were used to determine the best fit isotherm. By far, best results were obtained for the Temkin adsorption isotherm.

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Figure 4.10 Vs log c for Mild Steel



Figure 4.2 log K Vs 1/T for Temkin



Table 4.1Calculated values of E_a

Conc.(%)	E _a (kJ/mol)	\mathbb{R}^2
Acid	35.5026	0.9933
0.25%	13.0016	0.9673
0.5%	6.1374	0.9980
1.0%	0.4465	0.005

Figure 4.3 log Icorr vs 1/T

This is a straight line equation for log I_{corr} vs 1/T graph whose slope gives E_a and intercept gives the value of A. Table 4.1 gives the values of E_a . The lower value of activation energy in the presence of the inhibitor than in its absence reveals that the inhibitor is effective at higher temperatures and belongs to Putilova's third category of inhibitors. According to Dehri and Ozcan²⁶,Inhibitors whose IE% increases with temperature increase, the value of activation energy (E_a) found is less than that in the inhibited solution. It can be supposed that in such cases, specific adsorption of the products of the reaction between the inhibitor and the metal salt formed in the acid is possible, as well as adsorption of the inhibitor itself.

Table 4.2Slope, intercept, correlation coefficient values of the curves, Equilibrium constant and Gibbs free energy values for Polyvinyl Alcohol calculated from Temkin isotherm

Temp. (Kelvin)	Slope (-2.303/2a)	Intercept (-2.303 log K/2a)	а	R ²	К	∆G° _{ads} (kJ/mol)
308	0.2955	0.6373	-3.8967	0.9851	143.44	-23.0048
318	0.304	0.7672	-3.7878	0.9964	333.95	-25.9863
328	0.2375	0.8392	-4.8484	0.9077	3415.65	-33.1452
338	0.2425	0.899	-4.7484	0.9861	5095.84	-35.2801

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Large values of K imply more efficient adsorption and hence better inhibition efficiency. The ΔG_{ads} values are all negative²⁹, a clear indication that adsorption of the inhibitor onto the metal surface is spontaneous and the increase in values with rise in temperature shows that the spontaneity of the adsorption increased as temperature was raised. Generally, values of (ΔG_{ads}) up to - 20 kJmol⁻¹ are consistent with the electrostatic interactions between the charged molecules and the charged metal (physisorption)³⁰ while those around -40 kJmol⁻¹ or higher are associated with chemisorption as a result of sharing or transfer of electrons from polymer molecules to the metal surface to form a coordinate type of bond (which indicates chemisorption) The values of ΔG_{ads} listed in table 4.2 indicate the chemisorption ³¹ of Polyvinyl alcohol on the mild steel surface at higher temperatures. The adherence of this adsorption layer species ^(27,28)) and the negative values of 'a' are indication of repulsive interaction in the adsorption layer. The increase in the value of ΔG_{ads} with rise is a feature of chemical adsorption process and Temkin isotherm is actually a feature of chemical adsorption.

SEM Studies

The micrographs of mild steel specimen without polymer composite showed a large number of pits and cracks of aggressive owing to corrosion in the absence of the inhibitor²⁹, but in the presence of the inhibitor there was much less damage on the surface. This was attributed to the formation of a good protective film on the mild steel surface (Migaheda et al., 2011).



(3000 Magnification) Figure 5.1 SEM of Plain Mild Steel Surface



(3000 Magnification) Figure 5.2 SEM of Plain Mild Steel Surface in 1N H₂SO₄

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(3000 Magnification) Figure 5.3 SEM of Mild Steel Surface in presence of Polyvinyl alcohol

Quantum Chemical Calculations

Table 6 shows the optimized parameters of the inhibitors by using Hyperchem 7.5. Figure 6.1 shows the optimized geometry of the Polyvinyl alcohol molecule, figure 6.2 shows the charge distribution on the Polyvinyl alcohol molecule. Figure 6.3 and 6.4 shows ball and stick models and their various optimized parameters calculated are given in table 6.



Figure 6.1Optimized Geometry (PVA)



Figure 6.2 Charge distribution on (PVA)



Figure 6.3 Electrostatic potential surface Polyvinyl alcohol



Figure 6.4 HOMO of the (PVA)



Figure 6.5 LUMO of (PVA)

Table 6 Electronic and Energetic Parameters of Polyvinyl alcohol by using ZINDO/1 method

	Binding Energy (Kcal/mol)	Heat of formation (Kcal/mol)	HOMO (eV)	LUMO (eV)	ΔE (eV)	Dipole Moment (Debye)
Monomer	-1642.28	-1032.53	-9.3025	9.5805	18.8830	2.29
Monomer (Fe in space)	-1851.83	-1142.79	-6.5521	2.8091	9.3612	10.21
Monomer (Fe bonded)	-1821.64	-1112.61	-6.5433	2.7770	9.3203	10.05
Dimer	-3836.64	-2512.95	-9.4745	10.4887	19.9632	2.842
Dimer (Fe in space)	-4038.03	-2615.03	-6.1061	3.2899	9.396	10.59
Dimer (Fe bonded)	-4015.43	-2592.43	-6.0909	3.3612	9.4521	10.76
Tetramer	-7528.34	-4985.15	-6.9871	9.2962	16.2833	9.02
Tetramer (Fe bonded)	-7584.53	-5046.21	-4.9896	5.1305	10.1201	12.59
Octamer	-14932.98	-9950.80	-5.0083	8.2536	13.2619	25.5
Octamer (Fe bonded)	-15221.77	-10088.19	-3.9273	4.9643	8.8916	7.858

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According to the hard and soft acids and bases principle (HSAB principle), soft molecules have the HOMO orbital relatively higher in energy and the LUMO orbital relatively lower. This means that the HOMO-LUMO gap should decrease upon adsorption of the inhibitor on the metal surface^[30.31,32]. From these figures we can say that these figures actually give us an idea about the active site from where the adsorption on the metal takes place. It can be easily traced out that the donation is mainly through the heteroatoms i.e. nitrogen and oxygen.

Dipole moment values also give us an idea about the inhibition efficiency^{33,34}. Higher the value of dipole moment, higher is the extent of polarization, and greater is the tendency of donation of electrons. Therefore, we can say that greater is the dipole moment, greater is the inhibition efficiency.

Similarly, negative binding energy suggests that the inhibitor molecule is stable. More negative is the value of binding energy, more is the stability. The values of binding energy also indicate that the complex of metal – polymer is more stable than the free polymer molecule.

CONCLUSIONS

From the overall data and results of adsorption of Polyvinyl alcohol on mild steel in acid solution studied with the help of experimental and theoretical studies and confirmed by surface morphological techniques, the following conclusions have been drawn:

1. The Polyvinyl alcohol retards corrosion at ordinary temperatures and shows better inhibition efficiency at higher temperatures especially at 328 and 338 K. Therefore, its adsorption is not merely a physical or a chemical adsorption but a comprehensive adsorption.

2. The Polyvinyl alcohol shows no appreciable shift of E_{corr} towards any direction. This shows that this is a mixed type of inhibitors

3. There is an increase in the charge transfer resistance and decrease in the double layer capacitance in the inhibited solutions.

4. There is significant decrease in the i_c and i_p values in the presence of Polyvinyl alcohol and drop in the i_p and i_c values increases with increase in the concentration of the inhibitor.

5. The Temkin adsorption isotherm was found to be the closest to the description of the adsorption behaviour of the studied inhibitor supplemented by electrochemical studies.

6. The negative values of ΔG^{0}_{ads} along with high K_{ads} indicate a spontaneous adsorption process at all the temperatures but is most efficient at 328 K and 338 K. The values of enthalpy change and entropy change also reveal the same trend.

7. The images obtained from SEM clearly shows that the surface of mild steel corrodes more in the presence of $1.0N H_2SO_4$ and it is considerably reduced when Polyvinyl alcohol is added.

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