An electrochemical and theoretical evaluation of Polysorbate -40 as corrosion inhibitor of mild steel in sulphuric acid

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Abstract

Corrosion, an ongoing concern for industry, may cause reduced service life or directly impact the cost efficiency of the manufacturing process. Corrosion inhibitors can be used to prevent these problems. The corrosion inhibition effectiveness of Polysorbate - 40 on mild steel in 1 N H2SO4 was probed by using means of 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 Polysorbate -40 and increased with increase in the temperature with the highest efficiency being 88.6%. 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 (EHOMO), lowest unoccupied molecular orbital energy (ELUMO), energy gap (”E), dipole moment (¼) etc. have been found to supplement the results obtained from electrochemical measurements.

Keywords: Corrosion Inhibition, Polysorbate 40, Potentiodynamic and Potentiostatic Polarization; Electrochemical Impedance, Temperature Kinetics, Quantum Chemical Calculations; Surface Morphological Studies

1. 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 inhibitor[1-9]. In the present study, Polysorbate -40 is a polymer which enhanced the efficiency of the polymer solution as a corrosion inhibitor to a great extent. The improved inhibition efficiency is because of the following reasons.

a) Larger molecular area and weight which allows better absorption of the polymeric film on the surface of the metal.

b) The polymeric chain can displace the water molecules from the metal surface thereby lowering the entropy of the system.

c) The polymer has a multiple bonding sites which makes the desorption of the polymer a slow process leading to a stronger and effective polymeric film on the surface of the metal.

d) The polymers having cyclic rings and heteroatoms which have active centers of absorption and hence show better inhibitive properties.

2. Experimental

Electrode

Square (1cm x 1cm) mild steel 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 sonnicated with distilled water prior to immersion in the polarization cell..

Polysorabate-40 was prepared at three different concentrations (v/v) of 0.25%, 0.5% and 1%.

PotentiodynamicPolarization Studies

For electrochemical measurements, the cell used is a conventional three electrodes assembly in which platinum act as the counter electrode (CE), Saturated Calomel Electrode (SCE) as references electrode (RE) to which all potentials are referred and pre-fabricated mild steel coupon as Working

Electrode (WE).The potential of the metal electrode Vs saturated calomel electrode was measured with the help of a galvanostat having the range of 10mA to 100mA.For each run, a freshly prepared solution as well as a cleaned set of electrodes were used. Before recording the polarisation curves, WE were immersed in solution for 3 hours to establish their open circuit potential (OCP). The potentials were scanned from the OCP in the cathodic direction and subsequently in the anodic direction. In order to minimize ohmic contribution, the tip of Luggin capillary was kept close to WE. Polarisation measurements were made under the thermostatic conditions at 308K, 318K, 328K and 338K.All values reported were obtained from triplicate experiments. The inhibition efficiency is calculated using equation 1[10]

$$\eta_{GPS}\,(\%) = \left[\frac{Icorr_{Acid} - Icorr_{inhibitor}}{Icorr_{Acid}}\right] \times 100 \qquad (1)$$

Impedance Measurements

The EIS measurements were carried out using AC signals of amplitude 0.005mV peak to peak at the open circuit potential (OCP) in the frequency range 1,00,000–1 Hz. A potentio-scan type (CHI 760 Electrochemical Workstation) connected with a data acquisition system was used to conduct both the potentio-dynamic polarization, as well as the EIS-measurements.

Potentiostatic Polarisation Studies

Steady state Potentiostatic Polarisation was done through the potentiostat by applying potentials of 40mV increments after every one minute and the corresponding current values were recorded one minute after the potential was applied. The anodic polarization experiments were repeated for a number of times for each set and the reproducible data have been recorded here.

Temperature kinetics studies

The inhibiting effect of organic polymers on the metal corrosion in an aggressive medium is determined by their adsorbability at the electrode electrolyte interface.The surface coverage values obtained from the above-mentioned experimental studies were correlated with the concentration and temperature of the inhibitor. Different isotherms were then plotted, out of which Langmuir Adsorption Isotherm and Temkin adsorption isotherm were found to have the best fit with obtained surface coverage values. The value of equilibrium adsorption constant has evaluated from the intercept of the isotherm and consequently the values of the other thermodynamic parameters – ΔG_{ads}, ΔH_{ads} and ΔS_{ads} have been calculated. Further the corrosion current density obtained from galvanostatic polarization studies have been used to calculate Activation Energy in the presence and in the absence of the inhibitor. All these values so obtained from three distinct studies have been compared.

Surface Morphology

Polished specimens of Mild Steel, which had a smooth pit free surface were subjected to corrosion exposure using 1N H_2SO_4 and thereafter were exposed to various concentrations of inhibitors Polysorbate-40 (lowest and highest) to observe the extent of inhibition. They were then dried in a desiccator and subjected to a scanning electron microscope (SEM) examination.

Quantum Chemical Calculations

In the present investigation, Hyperchem 7.5 Release was used to create the initial geometries of Polyvidone The geometries of these inhibitors were fully optimized by using the MM+ (Molecular Mechanics) and then reoptimized by ZINDO1 with Polak Ribierre gradient method and the calculations for the various molecule parameters were performed through UHF method. The convergence limit for optimization with respect to the total energy was taken as 0.1 kcal.The values of binding energy, heat of formation, energy of HOMO and LUMO, point group and dipole moment have been evaluated from these calculations.

Results and Discussions

Potntiodynamic Polarisation Studies

Tafel plot is used to determine experimentally i_{corr} from which the corrosion rate is calculated.1N sulphuric acid solution containing various concentrations, 0.5%, 1.0% and 2%, of

Polysorbate-40 was used for polarization studies. Logarithm of current densities were plotted against corresponding potentials and various parameters, OCP, i_{corr}, βa and βc, and I% were calculated which are given in the table 1. Figures 1(a) to 1(d) give the cathodic and Anodic polarization curves for the solution at various temperatures.

Table 1clearly shows that the corrosion currents decrease in presence of inhibitor compared to acid and are lowest for the highest concentration of Polysorbate 40 i.e. 0.190 mAcm-2 for 2% at 318K. The inhibition efficiency increases with increase in the concentration[14,15] of the inhibitor. The efficiency of the inhibitor also increases with the increase of the temperature[13] the inhibition efficiency is highest 88.6% at 338K as compared to 60.1% at 308K for 2% of Polysorbate-40. 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[11, 12].

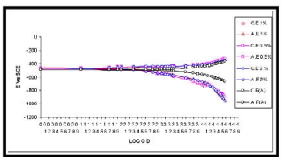


Fig.1 (a) Polysorbate-40 at 308 K

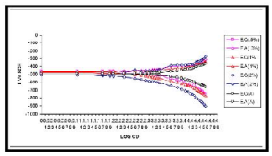


Fig.1 (b) Polysorbate-40 at 318 K

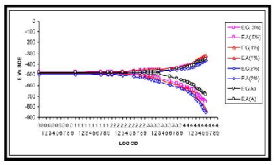


Fig. 1(c) Polysorbate-40 at 328 K

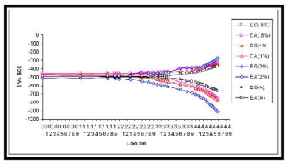


Fig.1(d) Polysorbate-40 at 338 K

The tafel slopes are almost constant, independent of the concentration of the inhibitor. There is drop in corrosion rate in the presence of polysorbate-40 which may be due to the adsorption of inhibitor molecules at the surface of mild steel through the hetero atoms i.e., O of C=O group.

Table 1 Corrosion Parameters of Mild Steel in 1N H2SO4 in the presence of Polysorbate 40

Conc. (mass%)	Temp. (Kelvin)	E_{corr}(-)mV	i_{corr} (mA.cm^{-2})	βc (mV/dec)	βa (mV/dec)	I %
H_2SO_4	308	510	1.000	140	40	
0.5		480	0.631	140	50	36.9
1		480	0.513	130	30	48.7
2		500	0.399	130	35	60.1
H_2SO_4	318	520	1.479	130	40	
0.50		440	0.561	120	60	62.0
1		480	0.384	120	40	74.0
2		470	0.19	190	80	87.1
H_2SO_4	328	510	2.454	60	20	
0.5		480	0.618	90	30	74.8
1		480	0.483	100	20	80.3
2		480	0.378	150	40	84.6
H_2SO_4	338	510	3.311	30	20	
0.5		470	0.788	90	60	76.2
1		470	0.462	80	50	80.0
2		465	0.377	100	30	88.6

There is no appreciable shift in the OCP values in uninhibited solutions and that of solutions having various concentrations of Polysorbate-40 at all temperatures. This indicates that this inhibitor behaves as mixed type inhibitor [11,12,16] 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 H_2SO_4 with and without Polysorbate 40 at 308 K are deduced from the analysis of Nyquist and Bode plots are given in Table 2. The intercept on the x-axis in the Nyquist plot gives the value of solution resistance, Rs and the end point on the same axis gives the value of Polarization Resistance, R_p.[17-20]

Then charge transfer resistance Rct can be calculated using the equation (2):

$$R_{ct} = R_p - R_s \qquad (2)$$

Double layer capacitance is then, calculated using the equation:

$$C_{dl} = \frac{1}{2\pi f_{max} R_{ct}} \qquad (3)$$

Where, fmax is the frequency at which Nyquist plot has its maxima.

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

Inhibitor	Rct (Ωcm^2)	f (Hz)	C_{dl} (Fcm^{-2})	I%
1N H_2SO_4	96.7	5.486	3×10^{-4}	
2.0% Polysorbate 40	271.1	3.742	1.5×10^{-4}	64.3

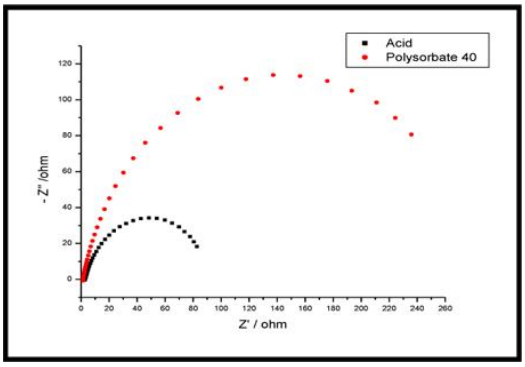


Fig. 2(a) Nyquist plot for acid and polysorbate 40 at 308 K

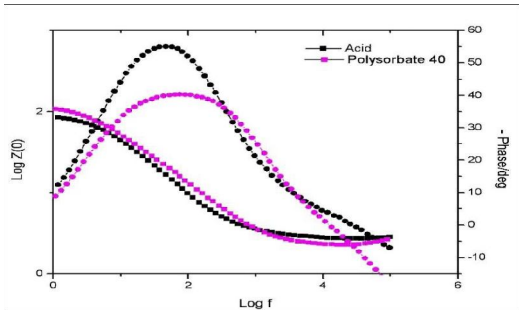


Fig.2(b)Bode plot for acid and polysorbate 40 at 308 K

Inhibitor can be associated with a decrease in capacitance of the metal. The decrease in Cdl in comparing with that in blank solution (without inhibitor), which can result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, suggests that the inhibitor molecules function by adsorption at the metal/solution interface [22,23].

Noticeably, the capacitive loops in both acids and in presence of inhibitor are not perfect semicircles which can be attributed to the frequency dispersion effect as a result of the roughness and inhomogeneous of electrode surface[21]. Furthermore, the diameter of the capacitive loop in the presence of inhibitor is larger than that in the absence of inhibitor which indicates that the impedance of inhibited substrate increases in presence of inhibitor.

By adding the inhibitor, R_{ct} value is increased. Generally, a large charge transfer resistance is associated with a slower corroding system.

Potentiostatic Polarisation studies

The steady state potentiostatic behaviour of the anodic dissolution of mild steel in 1N H_2SO_4 in presence of Polysorbate-40 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.

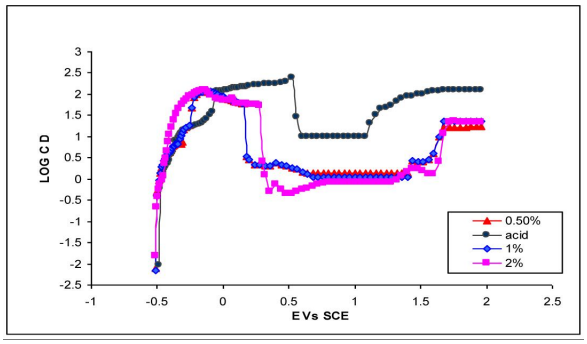


Fig.3 Potentiostatic Polarization curve for the Mild Steel in 1N H_2SO_4 in presence of various concentrations of Polysorbate-40

Table 3 Electrochemical parameters of anodic dissolution of mild steel in 1N H_2SO_4 in presence of Polysorbate-40

Solution	E_{pp}(mV)	$i_{critical}$ (mAcm-2)	i_p (mAcm-2)
1N H_2SO_4	590-1050	239.8	9.98
Polysorbate -40(0.5%)	600-1400	122.1	1.4
Polysorbate -40(1.0%)	680-1400	128.7	1.09
Polysorbate -40(2.0%)	480-1360	132.9	0.79

It is evident from the figure 3 that there is significant decrease in the ic and ip values in the presence of polysorbate-40. This suggests that the inhibitor is getting adsorbed thereby lowering the maximum current. The drop in the ip and ic values increases with increase in the concentration of the additive. The lowest values for ic and ip are observed at the concentration of 2.0%.The ip decreases from 9.98 mAcm-2 (in the presence of acid) to 0.79 mAcm-2 (in the presence of polysorbate-40). The ic value also drops from 239.8mAcm-2 (in the acid) to 132.9 mAcm-2 (in the presence of polysorbate-40).The stretch of passivation range increases with the increase in the concentration. The passivation range is also largest for 2.0% solution of polysorbate-40 i.e from 480-1360 mV. The lack of passivating character here is due to the non-uniform adsorption of these additives on the metal surface due to which a passive film is not formed.

Temperature Kinetic Studies

Inhibitors inhibit mainly by the process of adsorption24,25. The Adsorption Isotherm gives an insight into the adsorption mechanism and information on the metal-inhibitor interaction, and it can be derived from the curve of surface coverage rate against concentration of the inhibitor. Surface Coverage, ¸ is given by equation

$$\theta = \left[\frac{Icorr_{\text{Acid}} - Icorr_{Inhibitor}}{Icorr_{\text{Acid}}}\right] \qquad (5)$$

Attempts were made to fit ƒá 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,which has the form

$$e^{-2a\theta} = Kc \qquad (6)$$

Where 'a' is molecules interaction parameter, θ is the degree of surface coverage, K is equilibrium constant of adsorption process and 'C' is the concentration of the inhibitor.

Taking log on both sides,

$$\theta = -2.303\ (\log c)/2a - 2.303\ (\log K)/2a$$

In this isotherm ƒá is plotted against log c. From the intercept [2.303 (log K)/2a], value of K is calculated and 'a' is given by the slope [-2.303 / 2a].

Energy of activation is calculated by using the Arrhenius form, which is as follows:

$$K = Ae^{-Ea/RT} \text{ where,}$$

E_a is the activation energy for adsorption,A is the pre-exponential factor or Arrhenius constant.

K is the rate constant which is proportional to $I_{corr.}$.

Taking log on both sides

Log I_{corr} = log A - E_a/2.303RT

Fig.

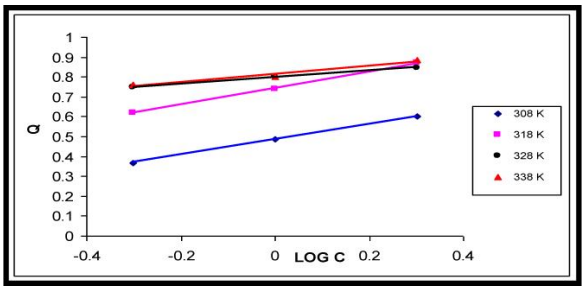


Fig.4(a) Curve fitting of the plot of θ against log c for Mild Steel

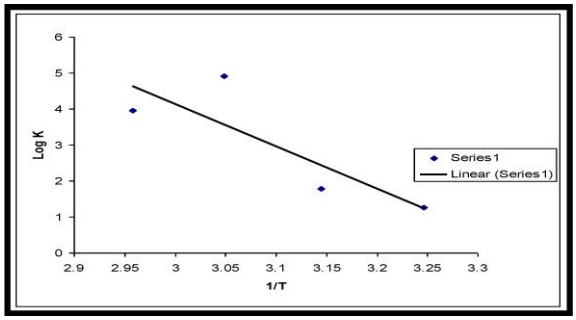


Fig4(b) the plot of the log K against 1/T for Temkin

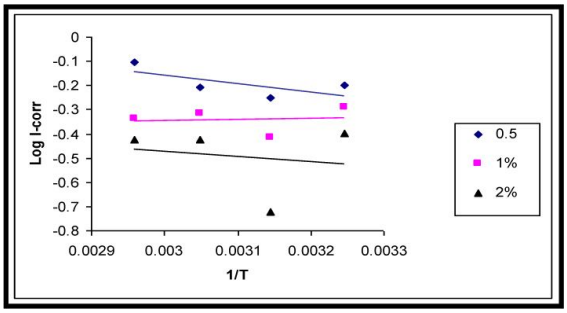


Fig.4(c) plot of log i_{corr} against 1/T for Mild Steel in 1N H_2SO_4 in the presence of Polyvidone

Table 4

Conc.(%)	E_a (kJ/mol)
Acid	35.5026
0.5%	4.0724
1.0%	8.3858
2.0%	6.4106

This is a straight line equation for log I_{corr} vs 1/T graph whose slope gives Ea and intercept gives the value of A. Table 4 gives the values of Ea.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 Ozcan[26], the relationship between the temperature dependence of percent inhibition efficiency (IE %) of an inhibitor and the activation energy found in its presence was given as follows: (a) Inhibitors whose IE% decrease with temperature increase, the value of activation energy (E_a) found is greater than that in the uninhibited solution; (b) Inhibitors whose IE% does not change with temperature variation, the activation energy (Ea) does not change with the presence or absence of inhibitors; (c) Inhibitors whose IE% increases with temperature increase, the value of activation energy (Ea) found is less than that in the inhibited solution. The fall in the value of E_a is probably accounted for by the increase in surface area of the metal covered by inhibitor molecules as temperature rises. 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.

The calculated values of molecular parameter 'a' are negative27, 28 in all the cases showing that repulsion exists in the adsorption layer. It is generally known that K denotes the strength between the adsorbate and adsorbent. Large values of K imply more efficient adsorption and hence better inhibition efficiency. The free energy of adsorption is related to the equilibrium constant of adsorption, K by the following equation:

$$\triangle G = -2.303\ RT\ [\text{Log } 55.5 + \text{Log } K]$$

The values of free energy of adsorption for polysorbate 40 in the temperature range 308K to 338K are shown in Table 5. The $\triangle G_{ads}$ values are all negative[29], 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

Table 5

Temp. (Kelvin)	Slope (-2.303/2a)	Intercept (-2.303 log K/2a)	a	R^2	K	$\Delta G°_{ads}$ (kJ/mol)
308	0.3853	0.4857	-2.98858	0.9999	18.22117	-17.7201
318	0.4167	0.7438	-2.76338	0.9994	60.95049	-21.4884
328	0.1628	0.799	-7.0731	0.9950	80883.96	-41.7767
338	0.206	0.8161	-5.58981	0.9539	9154.834	-36.9267

raised. (Bentiss et al. 2005). 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) (Hosseini et al., 2003). The values of ΔG_{ads} listed in Table 5 indicate the chemisorption[31] of polysorbate -40 on the mild steel surface at higher temperatures.

The adherence of this adsorption process to Temkin adsorption isotherm is suggestive of molecular interaction within the adsorption layer species [27,28] and the negative values of 'a' are indication of repulsive interaction in the 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 micrograph of mild steel specimen without polymer composite showed a large number of pits and cracks due to the attack of aggressive corrosive medium Fig.5(b). SEM micrographs of mild steel specimen in the presence of polyvidone illustrated a uniform layer formation on the metal surface Fig.5(c). (Athawal and Bhagwat, 2003). As shown in the SEM image, each unit has many polymer granules. This might be due to the multiple nucleation of polymer preferentially on the same site of the substrate. In some of the micrographs, it was possible to see a compact granular structure with few pores between the grains. This observation was similar to the report of polyaniline metal bilayer coating (Ananda Kumar et al., 2008). The resulting micrograph revealed that the surface was strongly damaged 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).

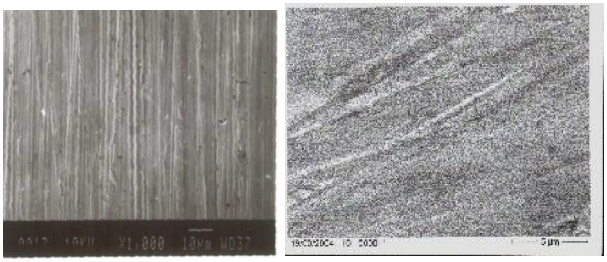


Fig 5(a)SEM of Plain Mild Steel Surface at 1000 and 3000 Magnification

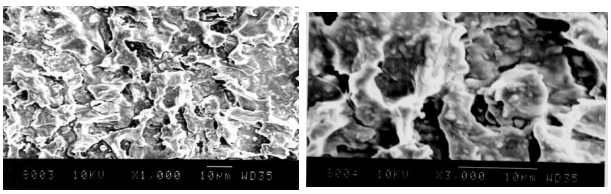
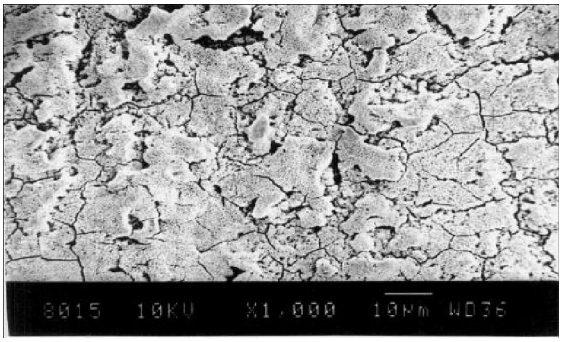


Fig.5(b)SEM of Plain Mild Steel Surface in 1N H_2SO_4 at 1000 and 3000 Magnification



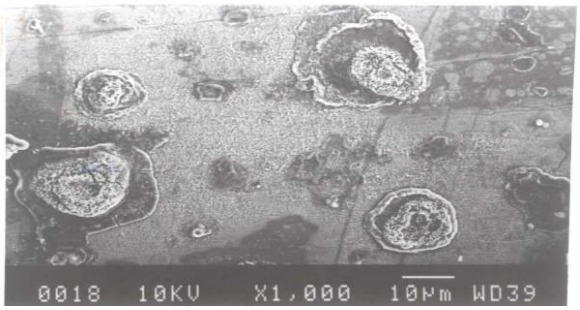


Fig5(c)SEM of Plain Mild Steel Surface in presence of 0.5% and 2% polysorbate 40 at 1000 Magnification

Quantum Chemical Calculations

Table 6 shows the optimized parameters of the inhibitors by using Hyperchem 7.5. Figures 6(a) shows the optimized geometery of the Polysorbate 40 molecule, figure 6(b) shows the charge distribution on the Polysorbate 40 molecule.Figure 6(d) and 6(e) shows ball and stick models and their various optimized parameters calculated are given in table 6.

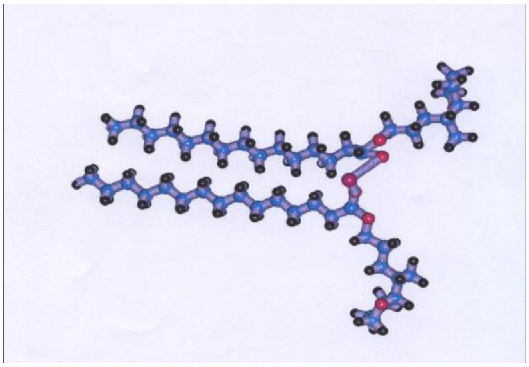


Fig.6(a) optimized geometery of the Polysorbate 40

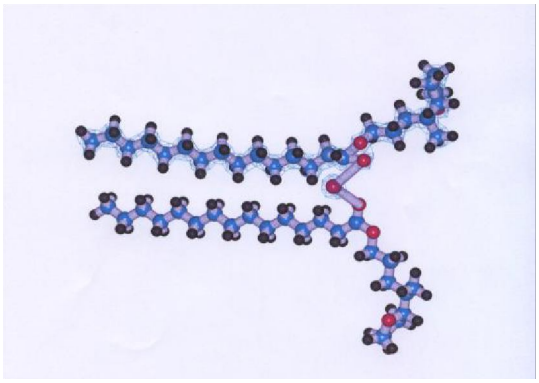


Fig.6(b) charge distribution on the Polysorbate 40

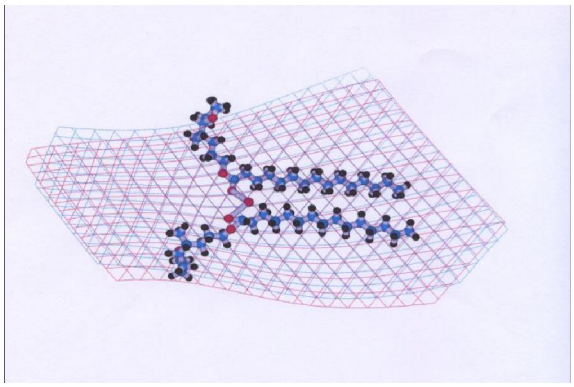


Figure 6(c) shows the electrostatic potential surface of Polysorbate 40 molecule.

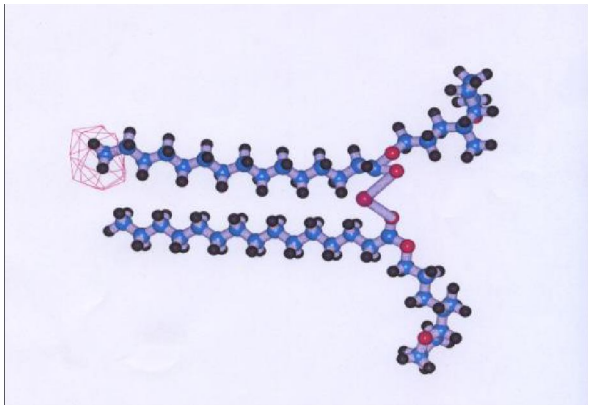


Figure 6(d) shows the HOMO of the Polysorbate 40

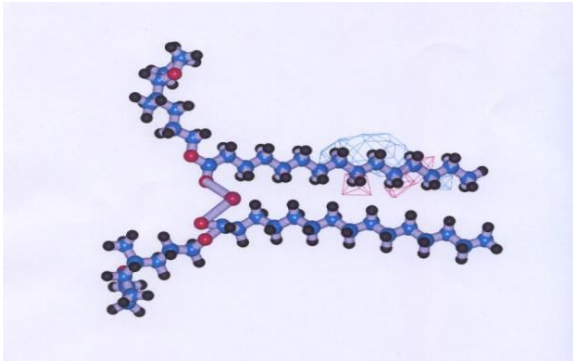


Fig6(e) shows the LUMO of the Polysorbate 40

The energy of the HOMO is directly related to the ionization potential and the energy of the LUMO is directly related to the electron affinity. The HOMO–LUMO gap, i.e. the difference in energy between the HOMO and LUMO, is an important stability index. A large HOMO–LUMO gap implies high stability for the molecule in chemical reactions [30.31,32] 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.

From these figures it can be easily traced out that the donation is mainly through the heteroatoms i.e. nitrogen and oxygen. Therefore, we can say that these figures actually give us an idea about the active site from where the adsorption on the metal takes place.Dipole moment values also give us an idea about the inhibition efficiency33,34. 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

The Heat of Formation and Binding Energy gives us an idea about the stability of an inhibitor. Positive heat of formation suggests that the formation of the inhibitor molecule is not spontaneous, as it requires energy for its formation. Therefore, it can split apart into its components on adsorption leading to lesser stability. Similarly, negative binding energy suggests that the inhibitor molecule is stable. More negative is the value of binding energy, more is the stability.

The adsorption of Polysorbate 40 on Fe takes place via the O of the –O-C=O (ester) group as the electron density is concentrated at O. It is evident from the data that the polymer has lower

Table 6 Electronic and Energetic Parameters of Polysorbate 40 using ZINDO/1 method

	Binding Energy (Kcal/mol)	Heat of formation (Kcal/mol)	HOMO (eV)	LUMO (eV)	ΔE (eV)	Dipole Moment (Debye)
Monomer	-20033.70	-13304.89	-8.2921	10.0910	18.3831	5.27
Monomer (Fe bonded)	-20278.77	-13450.65	-3.9607	3.5878	7.5485	14.82
Dimer	-39483.5	-26182.14	-3.0996	6.6454	9.7450	4.07
Dimer (Fe bonded)	-40154.21	-26649.35	-3.9328	3.6119	7.5447	8.85

energy gap and higher dipole moment; therefore it acts as efficient inhibitor. The values of binding energy also indicate that the complex of metal – polymer is more stable than the free polymer molecule.

Conclusion

From the overall data and results of adsorption of polysorbate 40 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 Polysorbate40 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 Polysorbate40 shows no appreciable shift of Ecorr 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 ic and ip values in the presence of polysorbate-40 and drop in the ip and ic 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 ”G0ads along with high Kads 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 Polysorbate 40 is added.

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