

Experimental Study of the Inhibition Efficiency of 3, 5 Substituted Piperidin-4-ones

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Abstract: The Corrosion Inhibition performance of Ethyl substituted Piperidones namely 3-Ethyl 2, 6-Diphenyl Piperidin-4-one (DPN) and 3, 5-Diethyl 2, 6-Diphenyl Piperidin-4-one (EDPN) on mild steel in 1M H₂SO₄ was studied by Weight loss measurement. The adsorption was spontaneous and followed Langmuir adsorption isotherm. Thermodynamic parameters were calculated for the adsorption process. The inhibition action of Piperidones is taking place by adsorbing on the metal surface in perpendicular direction using Nitrogen as anchoring site. The Nitrogen uses its lone pair of electrons with the vacant d orbital on the Fe-atoms. The inhibition efficiency of 3, 5-Diethyl 2, 6-Diphenyl Piperidin-4-one is comparatively more than 3-Ethyl 2, 6-Diphenyl Piperidin-4-one.

Keywords: 3-Ethyl 2, 6-Diphenyl Piperidin-4-one (DPN), 3, 5-Diethyl 2, 6-Diphenyl Piperidin-4-one (EDPN), Weight loss, Corrosion Inhibitor

1. Introduction

Corrosion is the loss of useful properties of a material as a result of environment on its surface. It affects both physical & chemical properties of metals. It also causes loss of metal resources all around the world. So awareness in control of corrosion is important.

In various corrosion control techniques acid pickling is widely used in industries to remove the rust on the metal surface. Inhibitors can also be used to prevent corrosion. The organic inhibitors found to be more efficient in these preventive techniques. The inhibiting action of the compounds is usually attributed to interactions with metallic surfaces by adsorption (Eddy et al 2009). S.A.Ali et al has synthesized bicyclic isoxazoline inhibitor solutions and is found to be good inhibitors on mild steel corrosion in synthetic brine. Quarshi et al (2003) showed that nitrogen and sulphur containing heterocyclic compounds are found to be excellent inhibitors in 1M H₂SO₄ solutions.

The aim of this work is to study the effect of corrosion inhibition by varying the position of substituent's in Piperidin - 4- ones. Weight loss measurements, effect of temperature studies were carried to study the mechanism of corrosion inhibition.

2. Materials and Methods

2.1. Mild Steel Specimen

Mild steel specimen used for this study has the following composition. C - 0.084, Si - 0.12, S - 0.021, Mo - 0.008, Mn - 0.037, P - 0.026, Cr - 0.020, Ni - 0.090. Mild steel specimen of size 2.5x2cm was employed for the weight loss measurements. A hole of diameter 0.5cm was drilled near the upper edge of the specimen in order to hook it on to the glass rod on immersion. The specimens were polished successively with emery papers 0, 1/0, 2/0, 3/0, 4/0 and 5/0

grades and degreased with Trichloroethylene. At the end of the period, specimens were taken out, washed well with running water, dried and finally weighed. Inhibition efficiency was calculated from the weight loss of specimens in the absence and presence of the inhibitor. The loss in weights was calculated at different temperatures from 303 – 333K.

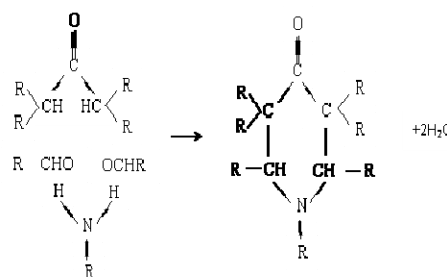
2.2. Acid

The bulk solution of 5N H₂SO₄ was prepared with double distilled water and was diluted to the required concentrations at the time of use. Dilute solutions were standardized before use.

2.3 Inhibitors used

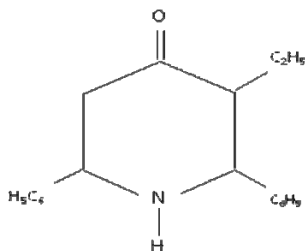
- 1) 3-Ethyl 2, 6-Diphenyl Piperidin-4-one (DPN)
- 2) 3,5-Diethyl 2,6-Diphenyl Piperidin-4-one (EDPN)

This Compound was prepared by following procedure of Mannich reaction.

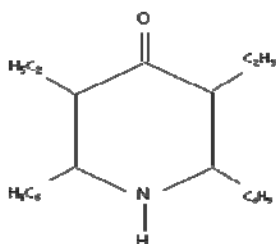


To a solution of dry ammonium acetate (9.8g, 0.125 moles) in methanol (30ml) benzaldehyde (29.0 g, 0.25 moles) and methyl propyl ketone (9.0g, 0.125 moles) was added. The mixture was just heated to boil and allowed to stand overnight at room temperature. Concentrated HCl (13ml) was then added; the precipitated hydrochloride was filtered

and washed with ethanol – ether (1:5). A suspension of the hydrochloride in acetone was treated with ammonia (1:1) and the free base was precipitated on dilution with excess water. Recrystallisation from ethanol gave the pure hydrochloride 16.0 g (40%) mp-233 to 255°C (Lit mp224 to 226°C).



3-Ethyl 2, 6-Diphenyl Piperidin-4-one (DPN)



3, 5-Diethyl 2, 6-Diphenyl Piperidin-4-one (EDPN)

3. Results and Discussion

3.1. Weight loss measurements

Table1 gives the values of inhibition efficiency for different concentrations of Piperidin -4 – ones in 1M H₂SO₄.

Weight loss measurements revealed that the corrosion inhibition efficiency of different substituted Piperidin – 4 – ones increases with increase in concentration. But 3, 5-Diethyl 2, 6-diphenyl Piperidin-4-one (EDPN) shows more inhibition efficiency than 3-Ethyl 2, 6-diphenyl Piperidin-4-one (DPN).

Table1. Values of inhibition efficiency for different concentrations of Piperidin-4-ones

Name of the inhibitor	Concentration 'C' (mM)	Weight loss (g)	Corrosion Rate (mmpy)	Inhibitor efficiency %	Surface coverage (θ)
3-ethyl 2,6-diphenyl Piperidin-4-one (DPN)	Blank	0.045	49.76	-	-
	0.1	0.038	42.19	15.21	0.1521
	0.25	0.034	37.62	24.38	0.2438
	0.5	0.029	32.5	34.68	0.3468
	1	0.024	26.6	46.53	0.4653
	2	0.021	23.6	52.57	0.5257
	3	0.02	22.04	55.7	0.557
	5	0.019	21.04	57.72	0.5772
3,5-diethyl 2,6-diphenyl Piperidin-4-one (EDPN)	Blank	0.045	50.2	-	-
	0.1	0.039	43.63	13.08	0.1308
	0.25	0.043	48.09	4.21	0.0421
	0.5	0.032	35.28	29.71	0.2971
	1	0.027	30.16	39.91	0.3991
	2	0.02	22.15	55.88	0.5588
	3	0.019	20.93	58.31	0.5831
	5	0.019	21.04	58.09	0.5809

The increase in inhibition efficiency with concentration is due to increase in surface coverage θ of the compounds on the mild steel surface. The adsorption therefore plays a role in inhibition. A plot of C/θ vs. C gave a straight line which

showed that the adsorption of the inhibitor obeyed the Languir isotherm (figure 1).

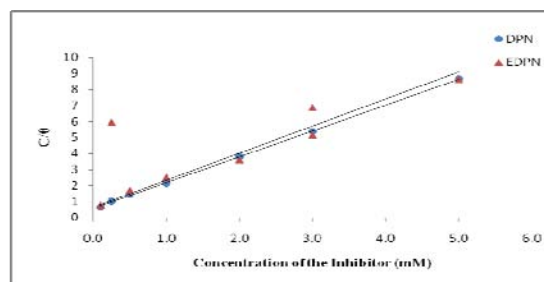


Figure1.Langmuir isotherm plot

3.2 Influence of Temperature and Thermodynamic parameters

Table 2 gives the inhibition efficiency values obtained by weight loss method at various temperatures. It is evident that inhibition efficiency decreases with temperature. The decrease in inhibition efficiency is due to desorption and dissolution of inhibitors in the aggressive medium. The Arrhenius plots for the corrosion rate of mild steel with the inhibitors in 1M H₂SO₄ are shown in figure 2.

Table 2. Values of inhibition efficiencies and corrosion rate for different temperatures in the presence of 5mM concentration of Piperidin-4-ones in 1M H₂SO₄.

Name of the inhibitor	Temperature (K)	Weight loss (g)	Corrosion Rate (mmpy)	Inhibitor Efficiency %
3-Ethyl 2,6-Diphenyl Piperidin-4-one (DPN)	298	0.0189	21.0374	57.72
	313	0.0317	35.2849	62.92
	323	0.0445	49.5324	65.61
	333	0.0929	103.4058	55.23
3,5-Diethyl 2,6-Diphenyl Piperidin-4-one (EDPN)	298	0.0188	20.926	58.31
	313	0.053	58.9936	35.44
	323	0.0717	79.8084	44.59
	333	0.1148	127.7825	44.67

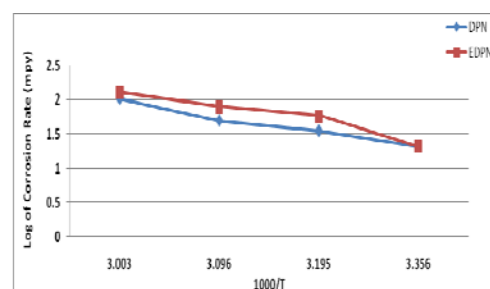


Figure 2.Arrhenius plots for mild steel in 1M H₂SO₄ in the presence of 5mM concentration of Piperidin-4-ones at different temperatures

The E_a values (calculated using Arrhenius plots) for the diethyl substituted inhibited solutions are greater than that of mono substituted Piperidin – 4 – ones. This indicates that the corrosion reaction of mild steel is retarded effectively by the presence of alkyl groups.

Table 3. Activation energies (E_a) and free energy of adsorption (ΔG_{ads}) for mild steel in the presence of Piperidin-4-ones in 1M H_2SO_4

Name of the Inhibitor	Temperature (K)	3-Ethyl 2,6-diphenyl Piperidin-4-one (DPN)	3,5-Diethyl 2,6-diphenyl Piperidin-4-one (EDPN)
E_a at various temperature K ($kJ/mole^{-1}$)	298-313	26.74	53.59
	298-323	27.42	42.86
	298-333	37.54	59.72
$-(\Delta G_{ads})$ at various temperature ($kJ/mole^{-1}$)	298	-23.20	-24.46
	313	-24.31	-25.61
	323	-25.07	-26.42
	333	-13.81	-27.22

The negative value of ΔG_{ads} indicates the spontaneous adsorption of inhibitor on metal surface.

3.3. Mechanism of Inhibition

Analysis of the surface coverage results presented in Tables and for the piperidones reveals that the degree of surface coverage θ increases with increase in inhibitor concentration. This observation suggests that the mechanism of inhibition is basically an adsorption mechanism.

A brief review of literature would thorough enough light in this direction. It has been stated by Sankarapabavinasm et al that thionones with structural resemblance to Piperidones adsorb through the anchoring site 'S' atom with a perpendicular orientation to the metal surface {Fig 3}. Muralitharan et al have suggested that 3-methyl 2,6 diphenyl piperidone adsorbs through perpendicular orientation of piperidone to the mild steel surface.[Fig 4] Again Mallika et al have also proposed the similar mechanism for a series of Piperidones. On the basis of these above averments in can be concluded for the present work that the Piperidones taken for investigation also inhibit corrosion by adsorbing on metal surface in perpendicular orientation using nitrogen as anchoring site.

In this mechanism, the nitrogen uses its lone pair of electrons with the vacant d orbital on the Fe – atoms.

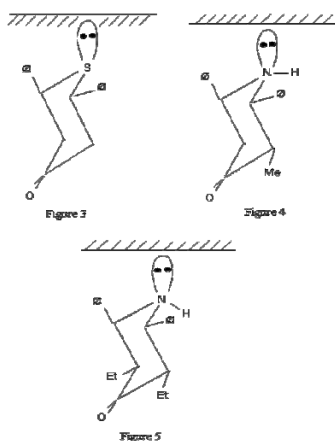


Figure 3

3.4.Reactivity of Piperidones

With the mechanism of inhibition of Piperidones have been fixed the reactivity of Piperidones and the consequent difference in inhibition efficiency could be explained by the structural difference between the Piperidones. The observed order of efficiency reveals that 3,5 – Diethyl 2,6 – Diphenyl Piperidin-4-one (DPEN) is more reactive than 3-Ethyl 2,6-diphenyl Piperidin – 4 – one (EPN).

The observed order suggests that substitution in 3,5 positions have affected the inhibition Efficiency. This must be obviously due to increased +I effect from two ethyl groups in 3 & 5 positions in EDPN which renders the anchoring N-atom more basic for interaction with metal surface than in EPN.

4. Conclusion

1. Inhibition efficiency of Piperidin – 4- one increases with increase in inhibitor concentration.
2. Inhibition efficiency of Diethyl substituted Piperidin – 4 –one is more than mono substituted Piperidin – 4 –one.
3. Temperature has significant effect on corrosion rate and inhibitor efficiency.
4. Adsorption of inhibitor on the metal surfaces follows Langmuir Adsorption isotherm.

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