

Inhibition of mild steel corrosion by oleochemical based hydrazides

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Selected hydrazides of fatty acids with C₉–C₁₇ carbon atoms have been synthesized and evaluated as corrosion inhibitors of mild steel (MS) in hydrochloric acid (HCl) solutions by weight loss and potentiodynamic polarization methods. The adsorption of all the hydrazides on mild steel surface in the acid solution has been found to obey Langmuir's adsorption isotherm. The potentiodynamic polarization studies revealed that all compounds block the corrosion reactions. Inhibition efficiency (IE) of these compounds has been found to vary with the concentration of the compound, solution temperature, immersion time and concentration of the acid solution. The values of activation energy (E_a) and free energy of adsorption (ΔG_{ads}) have been calculated to investigate the mechanism of the corrosion inhibition.

Keywords: Corrosion inhibition, oleochemical, hydrazines, mild steel, polarization.

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The use of corrosion inhibitors has increased considerably in recent years as awareness of corrosion has expanded. Organic compounds are widely used in various industries as corrosion inhibitors in acidic environments¹⁻³. Acid inhibitors find wide applications in the industrial field as a component in pretreatment composition, in cleaning solution for industrial equipments and in acidization of oil wells.

A perusal of literature reveals corrosion inhibitors derived from fatty acid constitute an important and potential class of corrosion inhibitors. However, very little work has been done on fatty acid derivatives as corrosion inhibitors⁴⁻⁶.

In continuation of the earlier work on the development of oleochemicals as acid corrosion inhibitors⁷⁻¹³, the authors have studied the corrosion inhibiting behaviour of fatty acid hydrazides, namely decanohydrazide (DH), dodecanohydrazide (DDH), hexadecanohydrazide (HDH) and octadecanohydrazide (ODH) on the corrosion of MS in HCl solutions.

Experimental Procedure

Inhibitors

The inhibitors were synthesized in the laboratory following the procedure described earlier¹⁴ and compounds were characterized through their spectral data and their purity was confirmed by thin layer chromatography (TLC). Name, structural formulas, melting points and molecular weight of the condensation products are given in Table 1.

Electrolyte

Analytical grade hydrochloric acid (Merck) and doubled distilled water were used for preparing test solutions for all the experiments. All the experiments were carried out, in 1 N acid solutions.

Specimens

The mild steel samples having composition, (Wt %): C, 0.14; Mn, 0.35; Si, 0.17; S, 0.025; P, 0.03% and balance Fe have been used for the experiment.

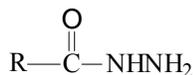
Weight loss studies

The mild steel sample of size 2.0 × 2.0 × 0.025 cm were used for weight loss measurement studies. Weight loss measurement studies were carried out at various temperatures ranging from 30 to 60 °C for various immersion times from 3 to 24 h. The experiments were performed as per ASTM method¹⁵.

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Table 1 — Name and molecular structures of the compounds used



1. R= CH₃(CH₂)₈ (Decanohydrazide, DH);
mol. wt=186.27; m p, 92-95 °C
2. R= CH₃(CH₂)₁₀ (Dodecanohydrazide, DDH);
mol. wt=214.32; m p, 113-14 °C
3. R= CH₃(CH₂)₁₄ (Hexadecanohydrazide, HDH);
mol. wt=270.43; m p, 78-79 °C
4. R= CH₃(CH₂)₁₆ (Octadecanohydrazide, ODH);
mol. wt=298.48; m p 81-82 °C

The inhibition efficiency (%) of the inhibitors was calculated by using the following equation:

$$\text{IE} = \frac{\text{CR}_0 - \text{CR}_i}{\text{CR}_0} \times 100$$

where

CR₀ = Corrosion rate of blank hydrochloric acid.

CR_i = Corrosion rate after adding inhibitors.

Electrochemical polarization measurement

For potentiodynamic polarization studies, mild steel strips of same composition, coated with commercially available lacquer with an exposed area of 1.0 cm² were used and the experiments were carried out at temperature (30 ± 1 °C). Equilibrium time leading to steady state of the specimens was 30 min. Sweep rate in potentiodynamic experiment was 1mV/sec. Potentiodynamic polarization studies were carried out using an EG & G Princeton Applied research (PAR) potentiostat/galvanostat (model 173), a universal programmer (model 175) and a X-Y recorder (model RE0089). A platinum foil was used as auxiliary electrode and a saturated calomel electrode (SCE) was used as reference electrode. Corrosion rate (CR) was calculated using the following formula¹⁶:

$$\text{CR} = \frac{0.13 \times I_{\text{corr}} \times \text{EW}}{D}$$

where,

I_{corr} = Corrosion current density in mA/cm².

EW = Equivalent weight of the metal in g/eq.

D = Density of the metal in g/cm².

Table 2 — Corrosion parameters for mild steel in 1 N HCl in absence and presence of different concentrations of various inhibitors from weight loss measurement at 30 °C for 3 h

Inhibitor conc. (ppm)	Weight loss (mg)	IE (%)	CR mean (mmpy)	SD
HCl	60.0	-	22.35	0.0
DDH				
100	10.7	82.1	3.90	0.43
200	9.7	83.7	3.55	0.26
300	8.3	86.1	2.90	0.06
400	6.9	88.5	2.46	0.28
500	6.4	89.3	2.34	0.34
DH				
100	20.3	66.2	7.44	2.49
200	15.3	74.5	5.66	0.35
300	11.7	80.5	4.24	0.35
400	11.2	81.3	3.99	0.48
500	9.6	84.0	3.46	0.74
HDH				
100	26.2	56.3	9.64	0.80
200	22.8	62.0	8.46	0.21
300	20.8	65.3	7.63	0.20
400	20.2	66.3	7.47	0.28
500	19.2	68.0	7.00	0.52
ODH				
100	27.3	54.5	9.95	0.73
200	24.0	60.0	8.84	0.17
300	21.9	63.5	7.99	0.25
400	21.6	64.0	7.95	0.27
500	21.0	65.0	7.74	0.37

Results and Discussion

Weight loss studies

The values of percentage inhibition efficiency (%IE) and corrosion rate (CR) obtained from weight loss method at different concentrations of inhibitors at 30 °C are summarized in Table 2. It has been found that all these compounds inhibit the corrosion of mild

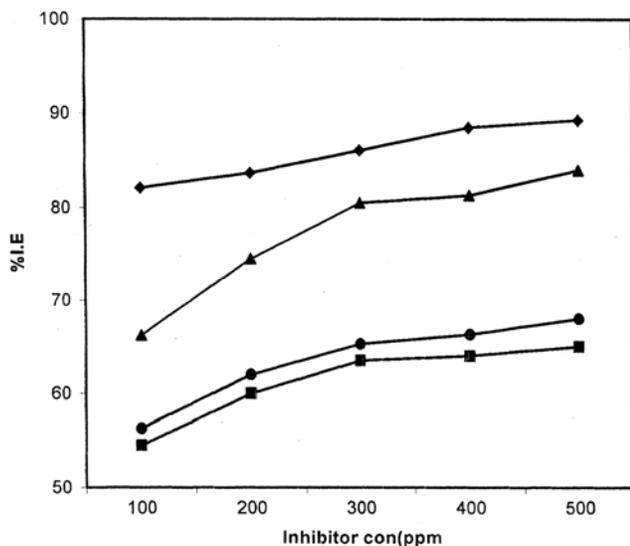


Fig 1 — Variation of inhibition efficiency with inhibitor concentration for 100-500 ppm concentration of inhibitors (◆-DDH; ▲-DH; ●-HDH; ■-ODH)

steel in 1 N HCl solution, at all concentrations used in this study i.e., 100-500 ppm. It has also been observed that the inhibition efficiency for all these compounds increased with the increase in concentrations (Fig. 1).

The variation of IE with solution temperature is shown in Fig. 2. It can be seen that IE for all of the compounds cause a significant increase with an increase in temperature from 30 to 40 °C. No significant change in IE has been observed for DH and DDH with the increase of temperature beyond 40-60 °C indicating that the inhibitive film formed on the metal surface is protective in nature at higher temperatures. HDH and ODH have been found to show decreasing IE trend for higher temperatures. The decrease in the IE for HDH and ODH may be attributed to the decomposition of the hydrophobic long carbon chain at higher temperatures.

The variation of inhibition efficiency of all the four hydrazides with the immersion time is shown in Fig. 3. It is observed that all the tested hydrazides show increase in the inhibition efficiency with the increase of immersion time from 3 to 24 h. This shows the persistency of the adsorbed fatty acid hydrazides over a longer test period.

From Fig. 4, it is clear that IE increases with increase in acid concentration up to 3 N HCl for all the hydrazides tested. Further increase in acid concentration up to 5 N HCl causes decreased IE for all the hydrazides except for DH. DH having C₉ has

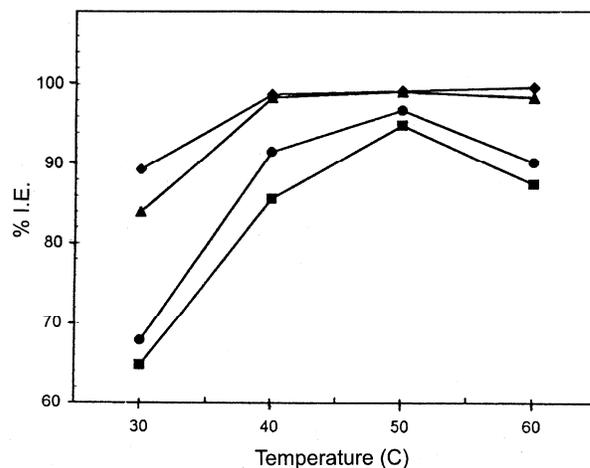


Fig. 2 — Variation of inhibition efficiency with solution temperature in 1 N HCl for 500 ppm concentration of inhibitors (◆-DDH; ▲-DH; ●-HDH; ■-ODH)

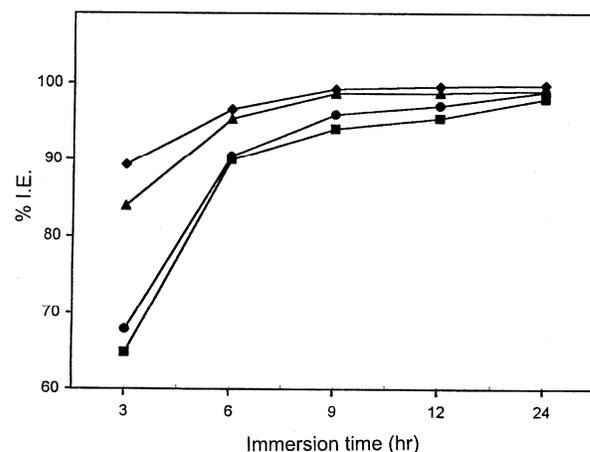


Fig. 3 — Variation of inhibition efficiency with immersion time in 1 N HCl for 500 ppm concentration of inhibitors (◆-DDH; ▲-DH; ●-HDH; ■-ODH)

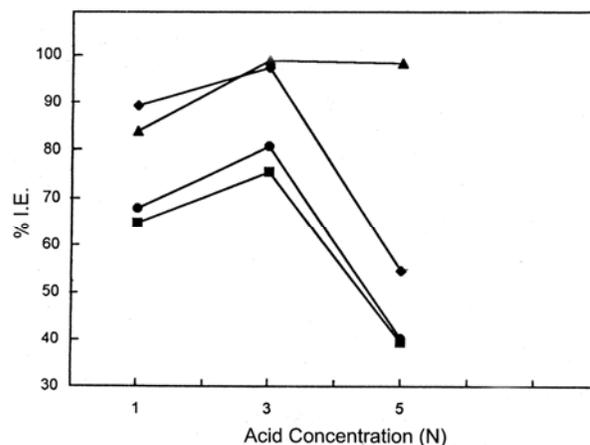


Fig. 4 — Variation of inhibition efficiency with acid concentration for 500 ppm concentration of inhibitors (◆-DDH; ▲-DH; ●-HDH; ■-ODH)

shown almost no change in IE with the increase in acid concentration from 3 N to 5 N HCl. The decrease in IE on increasing acid concentration beyond 3 N is due to increased aggressiveness of the acid¹⁷.

Application of adsorption isotherm

In order to understand the mechanism of corrosion inhibition, the adsorption behaviour of the organic adsorbate on the metal surface must be known. The degree of surface coverage (θ) for different concentration of inhibitors in 1 N HCl at 30 °C for 3 h of immersion time has been evaluated from weight loss values. The data were tested graphically by fitting to various isotherms. A straight line was obtained on plotting $\log (\theta / 1-\theta)$ versus $\log C$ (Fig. 5) suggesting, that, the adsorption of the compounds from HCl on mild steel surface follows Langmuir's adsorption isotherm.

Inhibition of corrosion of mild steel in the acidic solutions by the oleochemical-based hydrazides can be explained on the basis of molecular adsorption. It is apparent from the molecular structures that these compounds are able to get adsorbed on the metal surface through π -electrons of aromatic ring and lone pair of electrons of N- and O- atoms, and as a protonated species like amines¹⁸. The presence of long hydrophobic chain also plays a role in IE by preventing acid solution away from metal surface. Among the compounds investigated in the present study, the order of IE has been found as follows:

DDH > DH > HDH > ODH

(C₁₁) (C₉) (C₁₅) (C₁₇)

It has been observed that IE of the tested hydrazides increased with the increase in chain length up to C₁₁, the IE of DDH is greater than DH but on further increasing carbon atoms more IE decreases due to increase in steric hindrance, which lowers IE of HDH and ODH¹⁹.

The values of activation energy (E_a) obtained from Arrhenius equation^{20,21} and free energy of adsorption (ΔG_{ads}) calculated using the following relations are given in Table 3.

$$\Delta G_{ads} = -RT \ln (55.5 K)$$

and K is given by:

$$K = \theta / C (1 - \theta)$$

where θ is degree of coverage on the metal surface, C is concentration of inhibitor in mole/L, K is

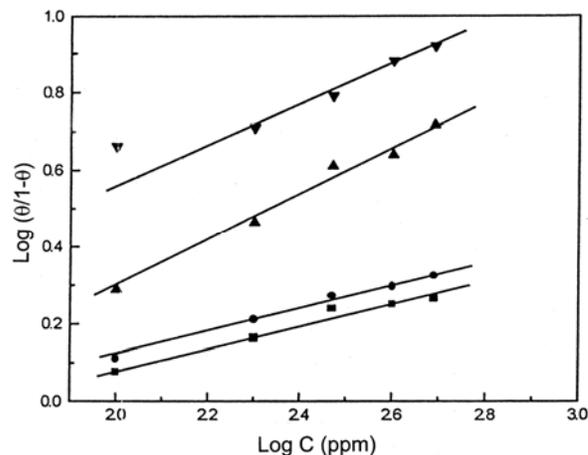


Fig. 5 — Langmuir's adsorption isotherm plots for the adsorption of various inhibitors in 1 N HCl on the surface of mild steel (▼-DDH; ▲-DH; ●-HDH; ■-ODH)

Table 3 — Activation energy (E_a) and free energy (ΔG_{ads}) for mild steel in absence and presence of maximal concentration of the inhibitor

Inhibitor conc. (ppm)	E_a (kJ.mol ⁻¹)	ΔG_{ads} (kJ.mol ⁻¹)			
		30 °C	40 °C	50 °C	60 °C
HCl	52.4	-	-	-	-
DDH	86.3	30.7	37.5	37.9	39.9
DH	74.3	29.5	36.7	39.9	39.1
HDH	74.1	26.9	30.8	34.8	33.2
ODH	66.9	27.2	32.4	36.1	32.9

equilibrium constant, R is a constant and T is temperature. It is found that the ΔG_{ads} value is less than -40 k J/mol (-9.56 k Cal/mol) indicating that the tested hydrazides of fatty acids are physically adsorbed on the metal surface²². The low and negative value of ΔG_{ads} indicated the spontaneous adsorption of inhibitor on the surface of mild steel²³. It was also found that value of activation energy of the inhibited systems were lower than that of uninhibited system. Putilova²⁴ has indicated that this type of inhibitor is effective at higher temperatures.

Potentiodynamic polarization studies

Various corrosion parameters such as E_{corr} , I_{corr} , IE and CR obtained from Fig. 6, by Tafel extrapolation method are given in Table 4. It is observed that presence of the hydrazides decrease I_{corr} values. Maximum decrease in I_{corr} was observed in case of DDH. The trend of the IE was found to be same as that of weight loss study. E_{corr} values do not show any

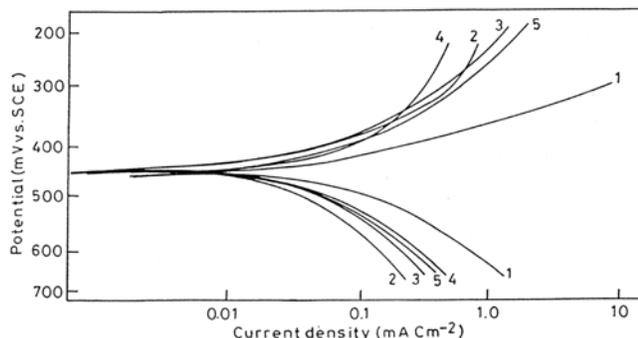


Fig. 6 — Potentiodynamic polarization curves of mild steel in 1 N HCl containing 500 ppm concentrations of various hydrazides (1) Blank (2) DDH (3) DH (4) ODH (5) HDH

Table 4 — Electrochemical polarization parameters for the corrosion of mild steel in HCl containing maximal concentration of various inhibitors at 30 °C

Inhibitor conc. (ppm)	E_{corr} (mV)	I_{corr} (mA cm^{-2})	IE (%)	CR (mmpy)
HCl	-458	0.36	-	6.65
DDH	-454	0.08	77.8	1.48
DH	-452	0.11	69.4	2.03
HDH	-456	0.13	63.9	2.40
ODH	-456	0.16	55.5	2.95

significant change in presence of all the hydrazides in the acid solution suggesting that all these hydrazides are mixed type inhibitors (*i.e.*, they retard the corrosion reaction by blocking both anodic and cathodic sites of the metal).

Conclusion

- (i) The acid hydrazides showed good performance as corrosion inhibitors in hydrochloric acid media.
- (ii) All of the four acid hydrazides inhibited corrosion by adsorption mechanism and the adsorption of these compounds from acid solution followed Langmuir's adsorption isotherm.
- (iii) All the compounds examined acted as mixed inhibitors.

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