



Corrosion is the degradation of metal or alloy by chemical or electrochemical reaction with its environment¹⁻². It is a major problem in several industries. It causes enormous economic wastage of metallic materials, which leads to heavy economic losses all over the world. The direct cost includes the replacement of corroded components, use of corrosion resistant alloys, use of coating and inhibitors etc. The indirect costs are loss of production during downtime, loss of products due to leakage, loss of efficiency, contaminations³⁻⁴ and sometimes it causes loss of human lives due to explosion/fire. The cost of corrosion can be reduced to an extent of 25% by applying some corrosion control techniques⁵. The prevalent corrosion control techniques are materials selection, proper design, electrochemical protection and use of inhibitors and paints/coatings. Among these methods, inhibitors are used in a wide range of applications, such as oil pipelines, domestic central heating systems, industrial water cooling systems and metal extraction plants. The advantage of corrosion inhibitor is that it can be implemented or charged *in situ* without disrupting a process and is also a cost effective method⁶. The major industries using corrosion inhibitors are the oil and gas exploration and production industry, the petroleum refining industry, the chemical industry, heavy industrial manufacturing industry, water treatment facilities, and the product additive industries. Due to ease of application and cost effectiveness, the use of inhibitors has increased manifold during the past several years.

Mild steel⁷ is one of the most important engineering metal, owing to its low cost and excellent mechanical properties. It is widely used as a

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construction material. In petroleum refineries⁸ mild steel is used for the construction of components in fractionation tower, separator drums, heat exchangers shell and tubes, reactor cladding, tubes in furnaces, piping and reboiler tubes etc. The mild steel is severely attacked in acid solutions by hydrogen sulfide, hydrochloric acid, hydrofluoric acid, sulfuric acid, and caustic in oil sector during processes related to drilling and distillation.

The research work described in the thesis deals with the study on some oxygen, nitrogen and sulfur containing heterocyclic organic compounds namely hydrazides, thiosemicarbazides, and imidazolines, triazoles and oxadiazoles derivatives as corrosion inhibitors for mild steel in 1.0 mol dm^{-3} HCl. The name, abbreviation and structure of the studied compounds are given in Tables 1- 2. The techniques such as weight loss, potentiodynamic polarization, electrochemical impedance and scanning electron microscopy were employed for the evaluation of inhibitive properties of hydrazides, thiosemicarbazides, imidazolines, triazoles and oxadiazoles on corrosion inhibition.

The thesis has been divided into six chapters. The first chapter describes the general introduction on corrosion, mechanism of inhibition, corrosion process in refinery and statement of the problem. The introduction also highlights the economic and technological importance of corrosion in *refineries*.

The materials used and the experimental conditions for the study are given in Chapter 2. The techniques namely, weight loss, potentiodynamic polarization, electrochemical impedance and scanning electron microscopy

used for investigating corrosion inhibition behaviour have also been discussed in Chapter 2. The method for the synthesis of inhibitors alongwith their characterization details are given in this chapter.

The third Chapter describes the results and discussion on the observed inhibition efficiency of hydrazides and thiosemicarbazides. The dependance of inhibition efficiency on [inhibitor], temperature, immersion time and [acid] are presented graphically in Figure 1 (for hydrazides) and Figure 2 (for thiosemicarbazides). The various thermodynamic parameters⁹⁻¹¹ were determined by using the following relations and the values are given in Table 3.

$$\text{Log (CR)} = \frac{-E_a}{2.303RT} + A$$

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

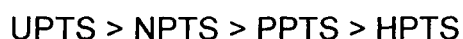
$$\text{CR} = \frac{RT}{Nh} \exp\left(\frac{\Delta S}{R}\right) \exp\left(-\frac{\Delta H}{RT}\right)$$

$$t_{1/2} = 0.693/k$$

The values of corrosion density (I_{corr}), corrosion potential E_{corr} and inhibition efficiency¹² were determined with help of Tafel plots and these are given in Table 4. The values of R_t and C_{dl} calculated from Nyquist plot are presented in Table 5. From these studies it is evident that the corrosion inhibiting properties of fatty acid hydrazides is due to molecular adsorption to the metallic surface. These compounds are able to get adsorbed on the steel surface through lone pair of electrons of N and O- atoms. The long hydrophobic chain of hydrocarbon prevents corrosion by keeping acid solution

away from metal surface. The excellent performance of DDH is attributed to the presence of long hydrophobic chain of C₁₁. The increase in carbon atoms above than 11 decreases inhibition efficiency due to increased steric hindrance to adsorption¹³.

Among the investigated thiosemicarbazides, the order of inhibition efficiency has been found as follows



It has been observed that the inhibition efficiency of the tested thiosemicarbazides increased with the increase in chain length up to C₁₁. A further increase in chain length up to C₁₇ has been found to decrease the inhibition efficiency. UPTS showed highest inhibition efficiency among the studied thiosemicarbazides due to presence of long hydrophobic chain.

In Chapter 4, the dependence of inhibition efficiency on [inhibitor], temperature, immersion time and [acid] (Figure 3) have been discussed. The inhibition efficiency was found to be in following order:

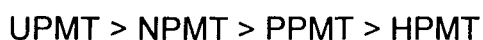


Inhibition efficiency of the studied imidazolines increased with the increase in chain length up to C₁₁. A further increase in chain length up to C₁₇ decreased the inhibition efficiency. The inhibitive effect of imidazolines is due to adsorption to the steel surface. The adsorption of imidazolines followed Langmuir adsorption isotherm. The thermodynamic parameters and observed data for electrochemical studies are given in Tables 3-5.

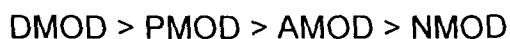
The studies on the inhibitive effect of triazoles and oxadiazoles are presented in Chapter 5. Figures 5-6 shows the dependence of inhibition

efficiency on [inhibitor], temperature, immersion time and [acid] of triazoles and oxadiazoles, respectively. Table 3-5 gives the information about the various thermodynamic and electrochemical parameters. From these observed results it is inferred that aliphatic triazoles are more effective inhibitor than aliphatic and aromatic oxadiazole. The superior performance of triazoles as compared to oxadiazole derivatives can be attributed to the presence of an additional benzene ring and three nitrogen atoms in comparison with oxadiazoles which possess two hetero atoms (O and N).

The order of inhibition efficiency of triazoles is:



The inhibition efficiency of oxadiazoles are:



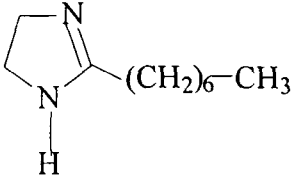
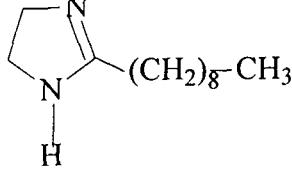
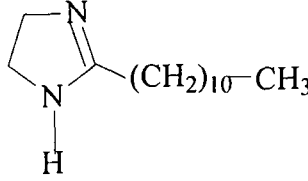
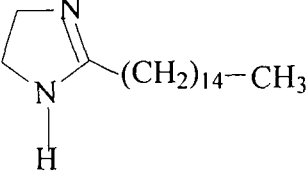
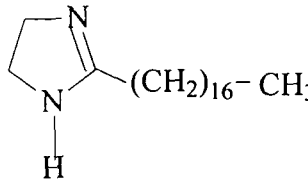
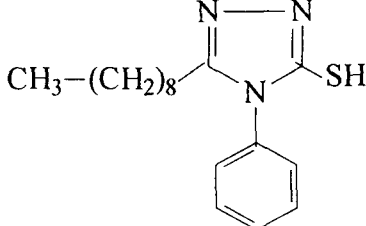
Chapter 6 describes the effect of anionic, cationic and nonionic surfactants of sodium dodecylsulfate (SDS), cetyltrimethylammonium bromide (CTAB), Triton-X-100 (TX-100), respectively on inhibition behaviour of 2-aminophenyl-5-mercapto-1-oxa-3,4-diazole (AMOD) and 2-Heptyl-1,3 imidazoline(HI). Inhibition efficiency of AMOD and HI increased appreciably in presence of surfactants¹⁴. The effect of inhibitor concentration, solution temperature, immersion time and acid concentration on inhibition efficiency of AMOD and HI were studied by weight loss method and potentiodynamic polarization studies. The dissolved surfactant helps inhibitor to adsorb onto the iron surface due to their hydrophilic property and leads to the strong bonding between the metal surface and inhibitor along with head group of surfactant¹⁵⁻¹⁶. The hydrophobic surfactant tails prefer to adsorb together to

form a coherent hydrophobic film that serves as a barrier to block the reaction between the iron surface and the external environment, thus inhibits the corrosion reaction between the metal and aqueous medium is inhibited. Further, the surfactant and inhibitor molecules inhibit the dissolution of metal either by blocking the cathodic or the anodic reaction of metal by occupying reactive sites, or by simply providing resistance to the supply of oxidant or the transport of the reaction products. Thus, corrosion is inhibited more effectively with increasing surfactant concentration. At further high [surfactant] the inhibition efficiency is decreased due to increase in ionic concentration in the surface region by incorporation of more hydrogen ions as coions or counter ions¹⁷.

Table 1: Name, Abbreviation and structure of the studied compounds

S. No	Name of the compounds (Abbreviated)	Structure
1.	Decanohydrazide (DH)	$\text{CH}_3-(\text{CH}_2)_8-\overset{\text{O}}{\parallel}{\text{C}}-\text{NHNH}_2$
2.	Dodecanohydrazide (DDH)	$\text{CH}_3-(\text{CH}_2)_{10}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NHNH}_2$
3.	Hexadecanohydrazide (HDH)	$\text{CH}_3-(\text{CH}_2)_{14}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NHNH}_2$
4.	Octadecanohydrazid (ODH)	$\text{CH}_3-(\text{CH}_2)_{16}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NHNH}_2$
5.	1-Undecyl-4-phenyl thiosemicarbazide (UPMT)	$\text{CH}_3-(\text{CH}_2)_{10}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}-\text{NH}-\overset{\text{S}}{\parallel}{\text{C}}-\text{NH}-\text{C}_6\text{H}_5$
6.	1-Pentadyl-4-phenyl thiosemicarbazide (PPMT)	$\text{CH}_3-(\text{CH}_2)_{14}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}-\text{NH}-\overset{\text{S}}{\parallel}{\text{C}}-\text{NH}-\text{C}_6\text{H}_5$
7	1-Heptadecyl-4-phenyl thiosemicarbazide (HPMT)	$\text{CH}_3-(\text{CH}_2)_{16}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}-\text{NH}-\overset{\text{S}}{\parallel}{\text{C}}-\text{NH}-\text{C}_6\text{H}_5$
8	1- Nonyl -4-phenyl thiosemicarbazide (NPMT)	$\text{CH}_3-(\text{CH}_2)_8-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}-\text{NH}-\overset{\text{S}}{\parallel}{\text{C}}-\text{NH}-\text{C}_6\text{H}_5$

Table 2: Name, Abbreviation ,and structure of the studied compounds

S. No.	Name of the compounds (Abbreviated)	Structure
9.	2- Heptyl-1,3 imidazoline (HI)	
10.	2- Nonyl-1,3 imidazoline (NI)	
11.	2-Undecyl -1,3 imidazoline (UDI)	
12.	2- Pentadecyl-1,3 imidazoline (PDI)	
13.	2-Heptadecyl-1,3 imidazoline (HDI)	
14.	5-Nonyl-4-phenyl-3-mercapto -1,2,4 triazole (NPMT)	

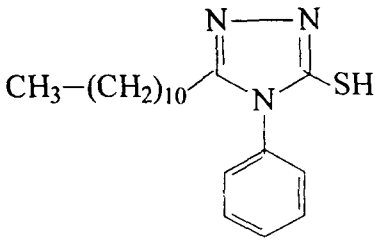
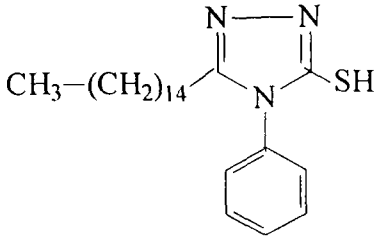
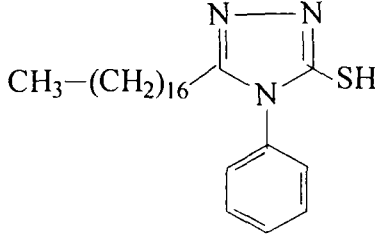
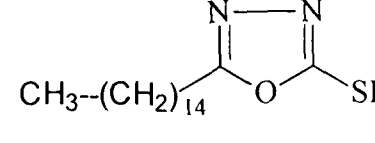
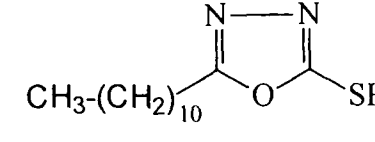
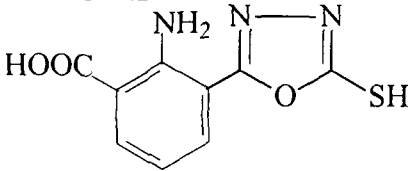
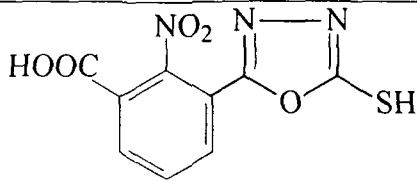
15.	5-Undecyl-4-phenyl-3-mercapto-1,2,4 triazole (UPMT)	$\text{CH}_3-(\text{CH}_2)_{10}$ 
16.	5-Pentadecyl-4-phenyl-3-mercapto-1,2,4 triazole (PPMT)	$\text{CH}_3-(\text{CH}_2)_{14}$ 
17.	5-Heptadecyl-4-phenyl-3-mercapto-1,2,4 triazole (HPMT)	$\text{CH}_3-(\text{CH}_2)_{16}$ 
18.	2-Pentadecyl-5-mercapto-1-oxa-3,4-diazole (PMOD)	$\text{CH}_3-(\text{CH}_2)_{14}$ 
19.	2-Undecyl-5-mercapto-1-oxa-3,4-diazole (UMOD)	$\text{CH}_3-(\text{CH}_2)_{10}$ 
20.	2-Aminophenyl-5-mercapto-1-oxa-3,4-diazole (AMOD)	
21.	2-Nitrophenyl-5-mercapto-1-oxa-3,4-diazole (NMOD)	

Table 3: Thermodynamic activation parameters for corrosion of mild steel in HCl in the absence and presence of inhibitors

System	E_a (kJ mol ⁻¹)	ΔH (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)	ΔG_{ads} (kJ mol ⁻¹)	$-Q$ (kJ mol ⁻¹)
HCl	51.18	48.56	200.40	-	-
DDH	86.3	40.32	248.34	36.26	33.02
DH	74.3	41.32	232.07	35.84	32.30
HDH	74.1	61.27	218.66	24.07	23.20
ODH	66.9	59.03	215.79	23.62	22.97
UPTS	75.23	77.88	198.56	39.75	28.72
NPTS	68.10	70.72	196.07	39.47	26.48
PPTS	58.32	60.95	195.31	38.88	19.78
HPTS	42.00	44.65	192.43	36.93	14.87
UDI	23.71	26.35	203.73	38.41	23.66
NI	24.76	27.40	202.20	37.12	23.04
PDI	23.77	32.42	196.75	36.25	18.08
HDI	29.75	32.39	192.43	35.81	18.62
HI	30.73	33.37	186.19	32.10	17.40
UPMT	63.73	40.32	241.60	36.26	30.02
NPMT	60.40	42.32	238.77	35.84	26.30
PPMT	55.53	28.30	235.90	24.07	21.20
HPMT	54.30	27.96	233.00	23.62	21.22
UMOD	55.04	80.03	220.58	34.90	30.43
PMOD	52.13	87.85	217.52	33.71	23.36
AMOD	51.12	101.41	215.98	30.24	18.02
NMOD	48.08	103.50	210.24	29.30	14.35

[Inhibitor] = 500 ppm; [HCl] = 1.0 mol dm⁻³; Time = 3 hours

Table 4: Electrochemical polarization parameters for the corrosion of mild steel in HCl containing inhibitors.

System	E_{corr} (mV)	I_{corr} (mAcm⁻²)	IE (%)
1N HCl	-461	0.360	-
DDH	-454	0.08	77.8
DH	-452	0.11	69.4
HDH	-456	0.13	63.9
ODH	-456	0.16	55.5
UPTS	-497	0.025	94.44
NPTS	-508	0.072	80.12
PPTS	-493	0.082	77.07
HPTS	-495	0.100	72.05
UDI	-480	0.033	90.83
NI	-476	0.037	89.72
PDI	-466	0.085	76.38
HDI	-479	0.120	66.66
HI	-493	0.150	58.33
UPMT	-492	0.004	98.78
NPMT	-490	0.002	94.49
PPMT	-487	0.048	86.77
HPMT	-485	0.082	77.22
UMOD	-552	0.027	92.50
PMOD	-533	0.031	91.38
AMOD	-526	0.036	89.85
NMOD	-517	0.045	87.52

[Inhibitor] = 500 ppm; [HCl] = 1.0 mol dm⁻³; Temp = 30°C

Table 5: Dependence of electrochemical impedance parameters on [UPTS] for mild steel in HCl.

System	R_t (ohm cm²)	C_{dl} (μF cm⁻²)	IE (%)
HCl	36	1511.50	-
DDH			
100	88.17	105.14	59.17
300	103.53	45.78	65.23
500	140.72	2.58	73.18
UPTS			
100	157.38	769.72	77.12
300	208.69	708.96	82.74
500	286.95	501.87	87.45
UDI			
100	86.95	946.84	58.48
300	141.30	776.92	74.45
500	304.34	315.22	88.13
UPMT			
100	223.07	105.14	83.78
300	346.15	45.78	89.57
500	392.30	27.58	91.07
UMOD			
100	139.13	769.72	74.11
300	167.64	708.96	78.52
500	243.47	501.87	85.15

[HCl] = 1.0 mol dm⁻³; Temp = 30°C

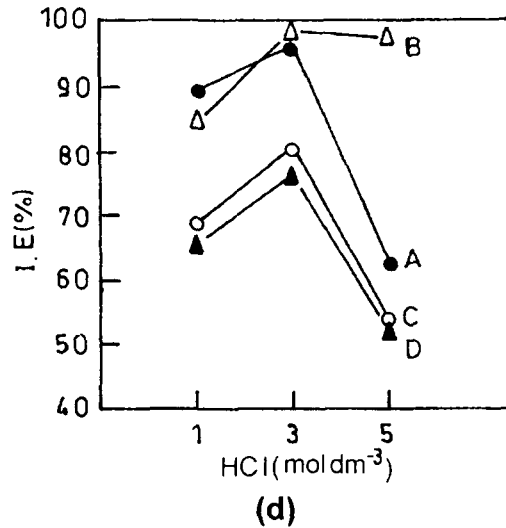
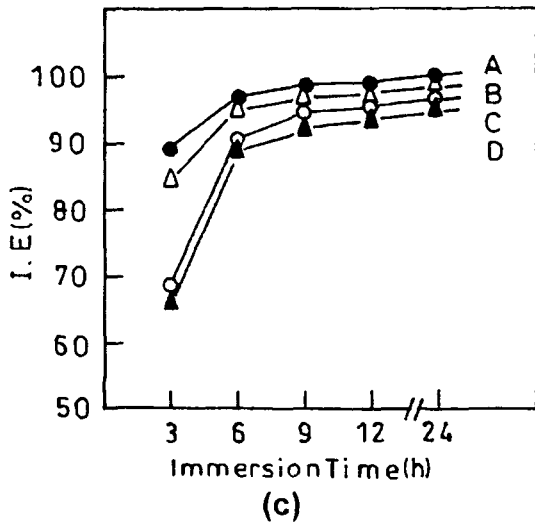
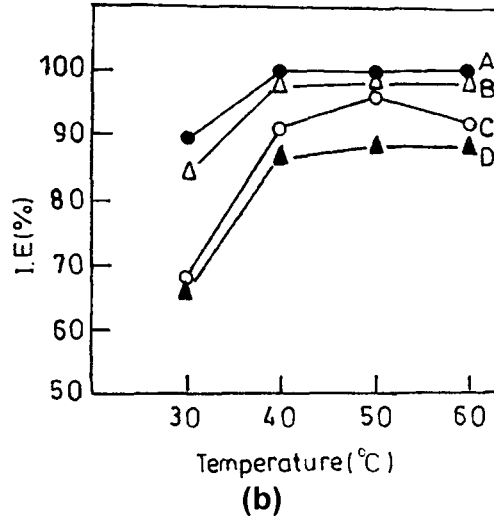
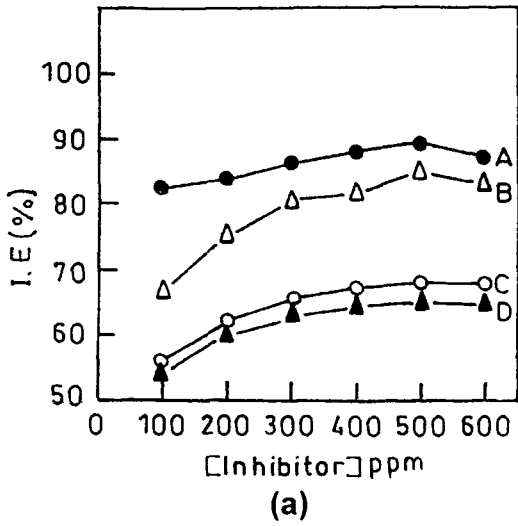


Fig. 1. Plot of variation of inhibition efficiency on (a) hydrazides concentration (b) temperature (c) immersion time and (d) [HCl] for the corrosion of mild steel in HCl.

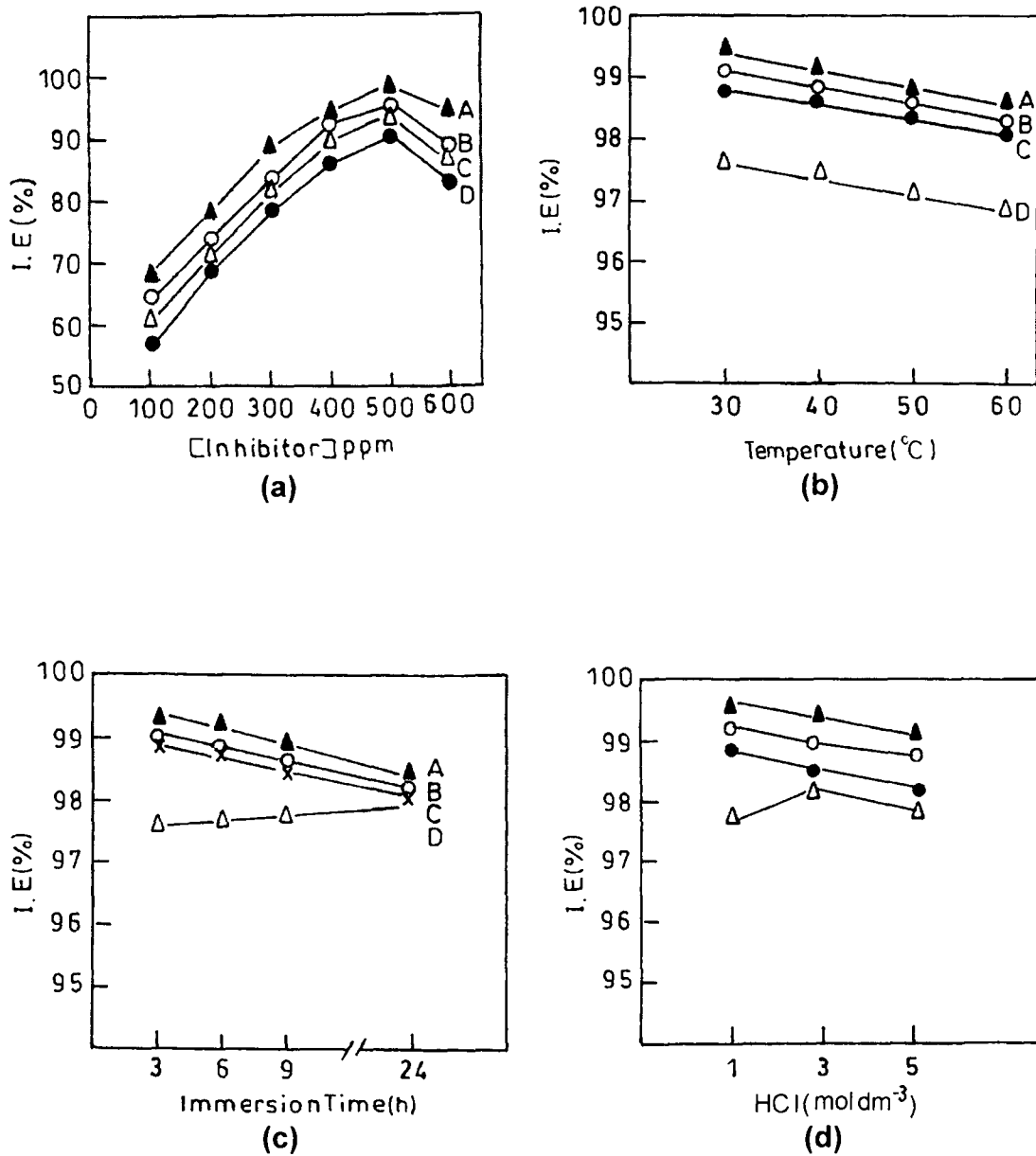


Fig. 2. Plot of variation of inhibition efficiency on (a) thiosemicardazides concentration (b) temperature (c) immersion time and (d) [HCl] for the corrosion of mild steel in HCl.

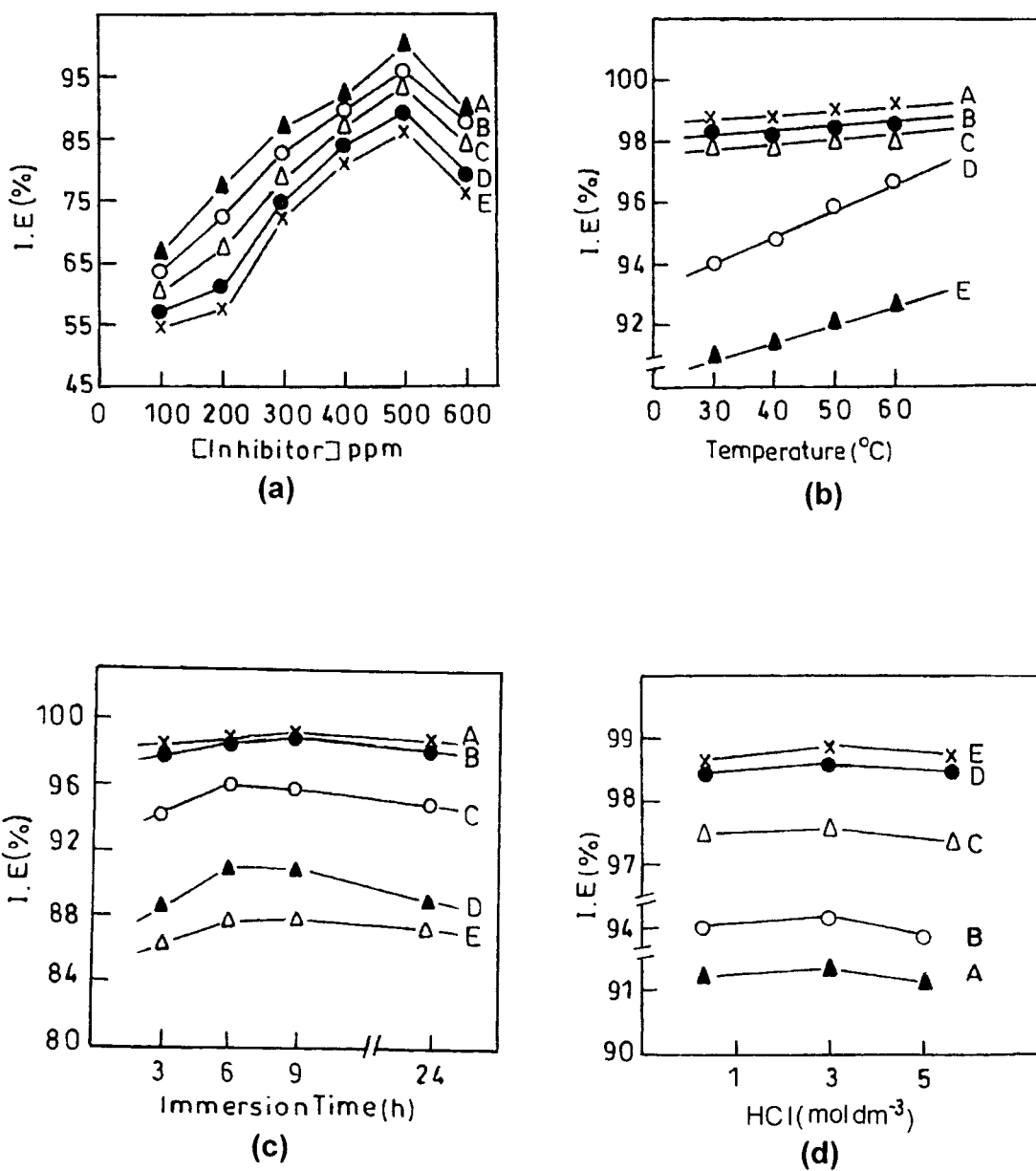


Fig. 3. Plot of variation of inhibition efficiency on (a) imidazolines concentration (b) temperature (c) immersion time and (d) [HCl] for the corrosion of mild steel in HCl.

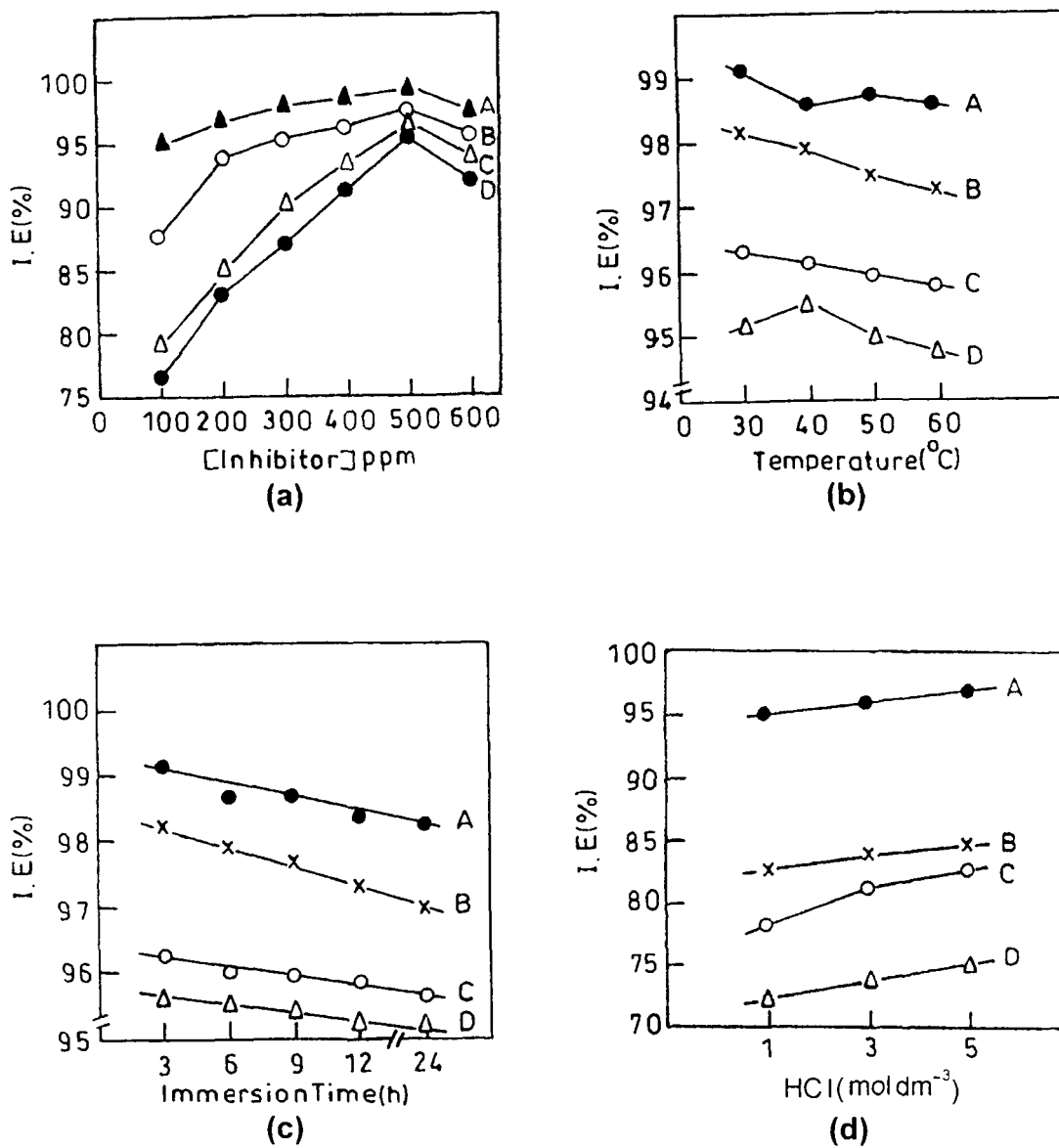


Fig. 4. Plot of variation of inhibition efficiency on (a) triazoles concentration (b) temperature (c) immersion time and (d) [HCl] for the corrosion of mild steel in HCl.

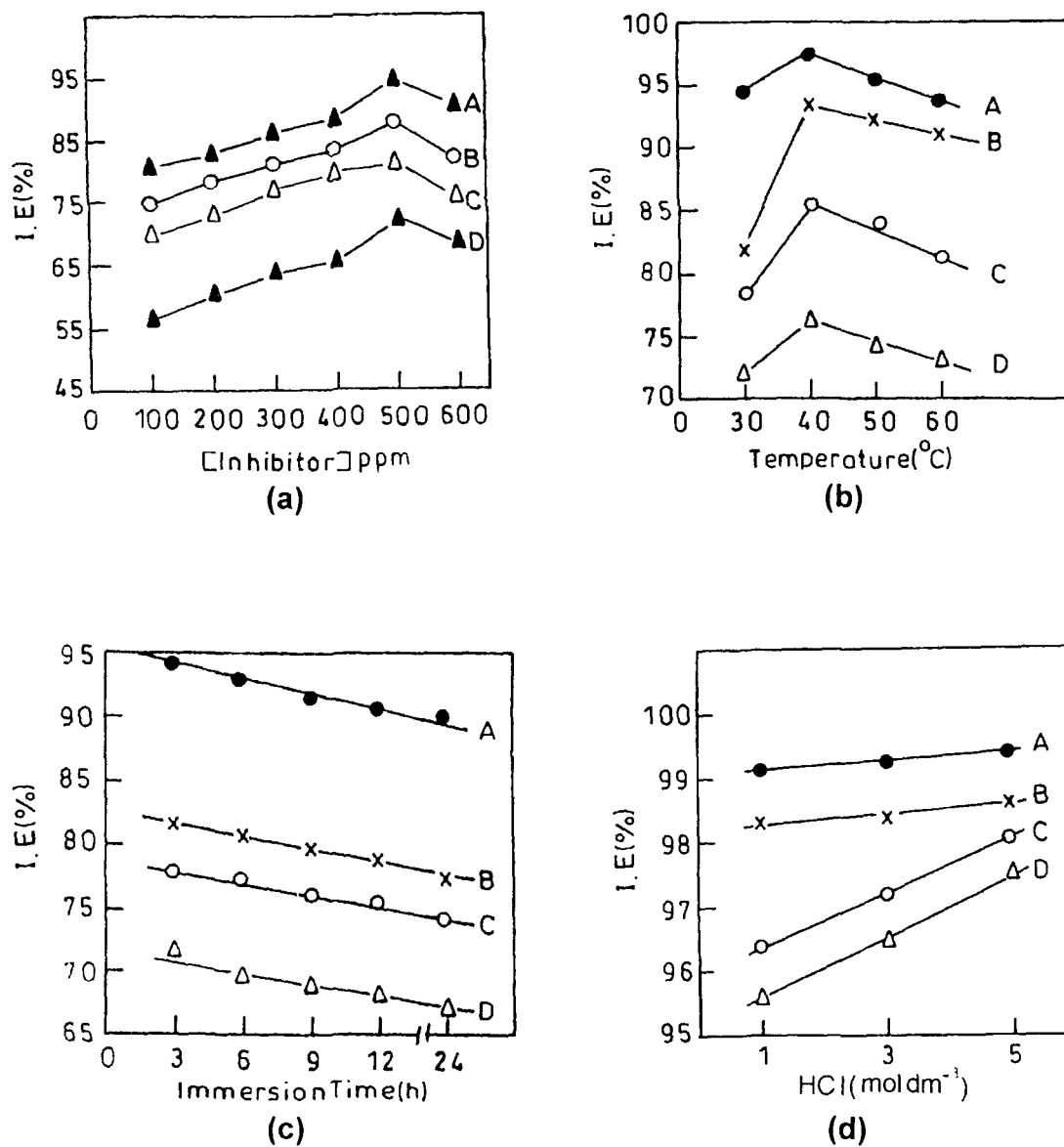


Fig. 5. Plot of variation of inhibition efficiency on (a) oxadiazoles concentration (b) temperature (c) immersion time and (d) [HCl] for the corrosion of mild steel in HCl.