A REVIEW ON MACROCYCLICS AS CORROSION INHIBITORS

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ABSTRACT

The available literature on the use of macrocyclic compounds as corrosion inhibitors has been reviewed. It has been noted that most of the work in this field has been done on porphyrin and phthalocyanine derivatives as corrosion inhibitors. The authors have synthesized a variety of macrocyclic compounds containing different heteroatoms such as O, N or S atoms and investigated their corrosion inhibiting characteristics. The salient features obtained from various studies such as weight loss, potentiodynamic polarization, electrochemical impedance studies, hydrogen permeation and auger electron spectroscopy studies have been discussed. The results of AES have suggested that macrocyclic compounds inhibit corrosion by adsorption mechanism. The inhibiting properties of these compounds have been explained in terms of molecular structure and synergism.

INTRODUCTION

Macrocyclic compounds have recently emerged as a new and potential class of corrosion inhibitors. Their ability to act as corrosion inhibitors is attributed to their fascinating molecular structure, the presence of π electrons or nonbonding electrons. In addition to these structural features planarity of these molecules further facilitates the formation of a strong bond between

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metal and macrocyclic molecules /1,2/. Porphyrins and phthalocyanines are two important types of macrocyclic compounds. The structure of these compounds is shown in Figure 1(a, b). Both the molecules contain four pyrrole rings. Porphyrins have –CH = bridging groups while phthalocyanines have –N = bridging groups.

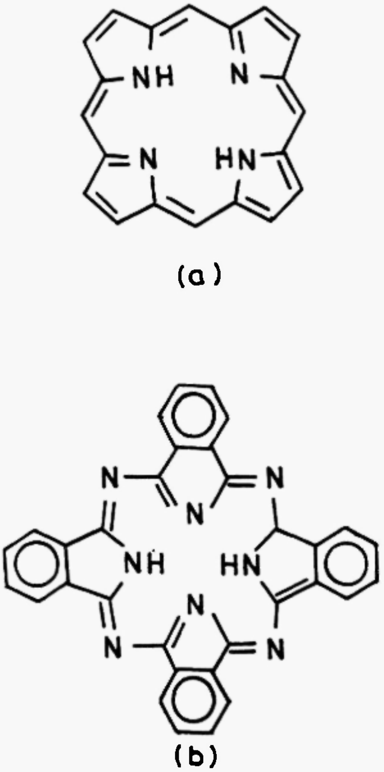


Fig. 1: Molecular structure of (a) porphyrin and (b). phthalocyanin.

Porphyrins as Corrosion Inhibitors

Agrawala and co-workers /3/ have studied the corrosion inhibitive properties of tetramethyl porphyrins (TMP) containing various counter ions such as iodide, chloride, benzoate, sulphate and toluene sulphonate on armco iron in 1% NaCl at 1mM conc. of the inhibitor. Tetramethylpyridyl-porphyrin

(TMPYP) containing toluene sulphonate and iodide ions showed high inhibition efficiency (IE, 76% and 80%) as compared to TMPYP containing other anions /4/. These authors have also observed that metalloporphyrins are better corrosion inhibitors than metal free porphyrins. TMPYP sulphonate incorporated with Fe(II) gave 96% inhibition efficiency (IE) while its metal free analogue gave only 76% IE.

Corrosion rate obtained on porphyrin vapour deposited iron coupons in 1% NaCl revealed that metal free porphyrins give higher inhibition efficiency than metalloporphyrins.

Potentiodynamic polarization studies were also conducted on porphyrin derivatives by these authors on iron sample containing vapour deposited TMPYP and TMPYP - toluene sulphonate in 1% NaCl. Both the compounds exhibited mixed type behavior.

Phthalocyanines as Corrosion Inhibitors

Hettiarachchi and co-workers /5/ explored the use of phthalocyanines and polyphthalocyanines as corrosion inhibitors in acid chloride environments. These authors believed that phthalocyanine would be a more effective corrosion inhibitor than porphyrins due to planarity of the molecules as well as the greater possibility of interaction between the π electrons of the macrocycle with conduction band of metal. Furthermore the planar molecule is expected to provide a high degree of coverage and hence a higher inhibition efficiency (IE). These authors considered that water soluble tetraaminophthalocyanine (TAPC) gave better inhibition than water insoluble tetrasulphophthalocyanine (TSPC). Polyphthalocyanines containing Fe(III) based inhibitor gave an IE as high as 82% as confirmed by both potentiodynamic and ac impedance analysis. Incorporation of long chain fatty acid further improved the IE of these compounds.

Pillai *et al.* /6/ found that the inhibition efficiency of cobalt tetrasulphatocyanine is greater than 78% even at a very low concentration ($2x10^{-4}$) in 2M HCl.

In the present article we have described the salient feature of our work on inhibiting properties of some macrocyclic compounds namely: 2,3,9,10-tetraphenyl-6,13-dithia-1,4,5,7,8,11,12,14-octaaza-cyclotetradeca-1, 3,6,8,10,13-hexaene (PTAT), 3,4,9,10-tetraphenyl-7,12-dithia-1,2,5,6,8,11-hexaazacyclobidecane-2,4,7,8,10,12-hexaene (PTAB), 3, 4, 9,10-tetraphenyl-7,12-dioxo-1,2,5,6,8,11-hexaazacyclobidecane hexaene (POAB), 2,5,10,13-

tetraoxo-1,6,9,14-tetraazacyclohexadecane (OAH), 7,8:15,16-dibenzo-2,5,10,13-tetraoxo-1,6,9,14-tetraazacyclo-hexadecane (BOAH), 7, 14-dimethyl-5, 12,dioxo-1,4,8,11-tetraazacyclotetradeca-1,7-diene (MOAT), 2,3:9,10- dibenzo-7,14-dimethyl-5,12-dioxo-1,4,8,11-tetraaza-cyclotetradeca-1,7,-diene (BMOAT), 3,4:11,12-dibenzo 2,5,10,13-tetraoxo-1,6,9,14-tetraaza-cyclohexadecane (DBOAD) and 3,4:7,8:11, 12:15,16-tetrabenzo-2,5,10,13-tetraoxo-1,6,9,14-tetraazacyclohexadecane (TBOAD) on corrosion of mild steel in acidic solution.

EXPERIMENTAL

Materials:

Mild steel strips having C = 0.14%, Mn=0.35%, Si=0.17%, S=0.025% P=0.03% and the rest iron were used for all experiments. For weight loss experiments mild steel strips of 2cm x 2cm x 0.25 cm and for potentiodynamic polarization, electrochemical impedance and hydrogen permeation studies mild steel strips with an exposed area of 1cm^2 were used.

Mild steel specimens were polished mechanically with emery papers of 1/0 to 4/0 grades and they were degreased subsequently with trichloroethylene ($CCl_2 = CHCl$) and dried at room temperature. Double distilled water and analytical reagent grade HCl & H_2SO_4 were used for preparing solutions. A mixture of 2% formic acid (HCOOH) + 10-12% acetone ($CH_3–CO–CH_3$) was used to dissolve the macrocyclic compounds. Inhibitors were synthesized in the laboratory following procedures reported previously /7/.

Molecular structure and other details of the inhibitors used in the present studies are given in Table-1.

Table 1

Name and structural formulae of the inhibitors used.

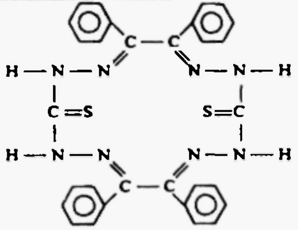
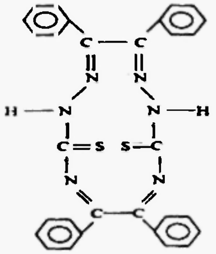
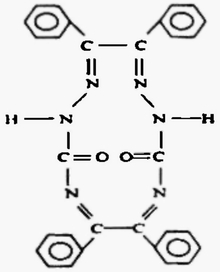
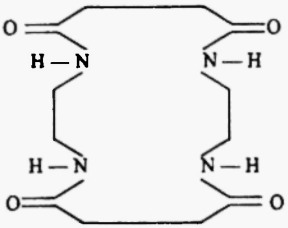
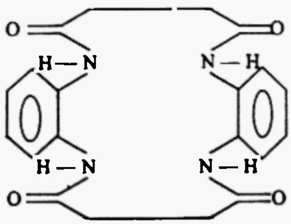
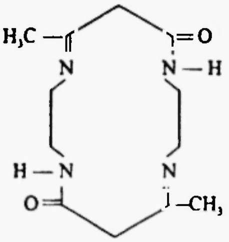
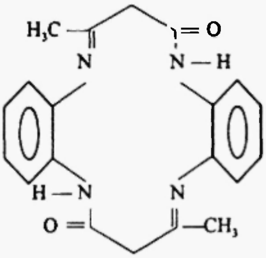
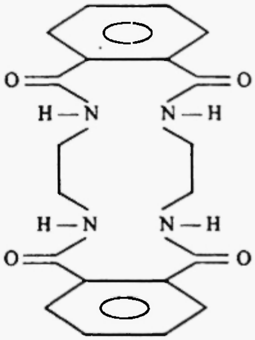
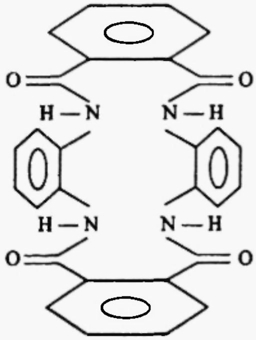
S.No.	STRUCTURAL FORMULA	DESIGNATION AND ABBRIVIATION
1		Tetraphenyl-dithia-octaazacyclotetradecane hexaene (PTAT)
2		Tetraphenyl-dithia-hexaazacyclobidecane hexaene (PTAB)
3		Tetraphenyl-dioxo-hexaazacyclobidecane hexaene (POAB)
4		2,5,10,13-tetraoxo-1,6,9,14-tetraazacyclohexadecane (OAH)
5		7,8:15,16-dibenzo-2,5,10,13-tetraoxo-1,6,9,14-tetraazacyclohexadecane (BOAH)

Table 1 (continued)
Name and structural formulae of the inhibitors used.

S.No.	STRUCTURAL FORMULA	DESIGNATION AND ABBRIVIATION
6		7,14-dimethyl-5,12-dioxo-1,4,8,11-tetaazacyclotetradeca-1,7-diene (MOAT)
7		2,3:9,10-dibenzo-7,14-dimethyl-5,12-dioxo-1,4,8,11-tetraazacyclotetradeca-1,7-diene (BMOAT)
8		3,4:11,12-dibenzo 2,5,10,13-tetraoxo-1,6,9,14-tetraazacyclohexadecane (DBOAD)
9		3,4:7,8:11,12:15,16-tetrabenzo-2,5,10,13-tetraoxo-1,6,9,14-tetraazacyclohexadecane (TBOAD)

Methods:

Weight loss studies:

Weight loss experiments were done according to ASTM methods described previously /8,9/ weight loss measurements for PTAT, PTAB and POAB were conducted in 1N, 3N and 5N HCl at 40°C for 3 hours. Corrosion inhibition tests were also carried out in 1N HCl and 1N H_2SO_4 for BMOAT, MOAT, TBOAD, DBOAD, BOAH and OAH at room temperature for 3 hours. The effect of temperature (40-70°C) and immersion period (24-96 hours) on the inhibition efficiencies of these compounds was also studied.

Potentiodynamic Polarization Studies:

Polarization curves were recorded potentiodynamically (1 mv/s) using an EG & G Princeton Applied Research (PARC) model 173 Potentiostat / Galvanostat, a model 175 universal programmer and a model REOO 89 X-Y recorder at 35°C ± 2°C. The cell assembly consisted of a mild steel as working electrode, platinum as counter electrode and Saturated Calomel Electrode (SCE) as the reference electrode.

Electrochemical Impedance Studies:

Nyquist plots for mild steel in 1N HCl containing 500 ppm concentration of three macrocyclic compounds viz.; PTAT, PTAB and POAB were recorded using an EG & G PARC model M 6310 system with M398 software at 30°+2°C.

Hydrogen Permeation Studies:

Hydrogen permeation currents were recorded using a strip chart recorder of a modified Devanathan - Stachurski two-compartment cell /10,11/ in the absence and presence of 500 ppm of PTAT and PTAB in 1N HCl.

Auger Electron spectroscopic (AES) studies:

AES studies were done on uninhibited and inhibited mild steel coupons with PTAT and PTAT + KI, using an Auger Electron Spectroscope (Varian CMA VT-112).

RESULTS AND DISCUSSION

The values of inhibition efficiency (IE) and corrosion rate (CR) for macrocyclic compounds (PTAT, PTAB and POAB) in 1N, 3N and 5N HCl are given in Table 2. The maximum inhibition efficiency of these compounds was found at 500, 700 and 2000 ppm in 1N, 3N and 5N HCl respectively. The influence of inhibitor concentration on IE of macrocyclic compounds in

Table 2

Corrosion parameters obtained from weight loss measurements for mild steel in 1N, 3N and 5N HCl containing different concentrations of macrocyclic compounds at 40°C for 3 hours

Inhi. Conc.(PPM)	PTAT		PTAB		POAB	
	I E (%)	C R (mmpy)	I E (%)	C R (mmpy)	I E (%)	C R (mmpy)
1 N HCl	–	16.81	–	16.81	–	16.81
25	63.80	6.08	52.40	7.98	45.00	9.24
50	67.40	5.47	57.40	7.15	53.30	7.84
100	74.50	4.27	64.00	6.03	61.30	6.50
200	76.80	3.90	71.50	4.78	68.50	5.29
300	79.50	3.43	76.80	3.90	74.30	4.31
400	80.10	3.34	79.00	3.52	75.10	4.17
500	81.40	3.11	79.20	3.48	78.10	3.66
3 N HCl	–	57.76	–	57.76	–	57.76
100	64.30	20.57	46.60	31.19	44.01	32.32
200	79.50	11.84	54.00	26.56	53.00	27.11
300	82.40	10.16	61.00	22.47	60.20	22.94
400	84.20	9.10	66.10	19.55	61.40	22.29
500	87.70	7.10	66.30	19.45	67.70	18.66
600	88.90	6.40	71.10	16.67	70.50	17.04
700	90.10	5.66	74.90	14.48	72.00	16.16
5 N HCl	–	139.49	–	139.49	–	139.49
500	52.20	66.59	32.60	93.94	30.00	97.56
700	57.80	58.74	40.00	83.58	36.00	89.20
1000	70.20	41.56	48.30	72.11	45.10	76.48
1500	80.40	27.25	59.90	55.86	55.10	62.36
2000	84.10	22.15	62.50	52.28	61.40	53.72

1N HCl has been illustrated in Figure 2(a). It is evident that IE increases on increasing the concentration of inhibitor and reaches maximum at optimum concentration of 500 ppm. The inhibition efficiencies of all three macrocyclic compounds followed the order:

PTAT > PTAB > POAB

This difference in their inhibitive action can be explained on the basis of their molecular structures. PTAT contains 10 heteroatoms (8 nitrogen and 2

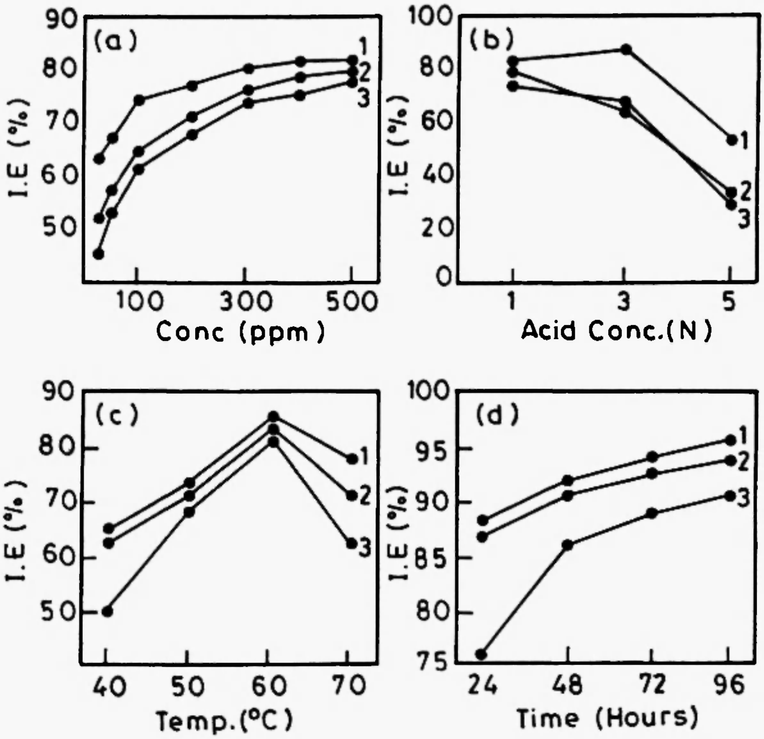


Fig. 2: Variation of inhibition efficiency with:-

(a) Inhibitor concentration (ppm) at 40°C in 1N HCl

(b) Concentration (N) of HCl containing 500 PPM of inhibitor at 40°C.

(c) Temp. (°C) in 1 N HCl containing 500 PPM of inhibitor.

(d) Immersion time (hours) at room temp. 35°C in 1 N HCl containing 500 PPM concentration of inhibitors.

1. PTAT 2. PTAB 3. POAB

sulphur) as reactive centers through which it adsorbs on the metal surface and gives an IE of 83%, while PTAB and POAB contain only 8 heteroatoms as reactive centers. Since compounds containing both nitrogen and sulphur atoms are reported to be better inhibitors than those containing nitrogen and oxygen atoms /12/. Hence PTAB (6 nitrogen and 2 sulphur atoms) gives better performance as corrosion inhibitors than POAB (6 nitrogen and 2 oxygen atoms) /13/.

The corrosion parameters obtained from weight loss measurements for different concentrations of TBOAD, DBOAB, BMOAT, MOAT, BOAH and OAH in 1N HCl and 1N H_2SO_4 are given in Table 3. It is seen from the table that IE increases with the increase in inhibitor concentration for all the compounds and reaches maximum at the optimum concentration of 1000 ppm for both acids (Figure 3(a, b)). The superior corrosive inhibitive behavior of TBOAD than that of DBOAD may be attributed to the presence of four aromatic rings. This facilitates greater adsorption of TBOAD on the metal surface than that of DBOAD which has only two rings /14/. The better performance of BMOAT and BOAH than MOAT and OAH is attributed to the presence of aromatic rings containing π electrons which facilitates greater adsorption than MOAT and OAH which do not have aromatic rings /15/. Desai *et al.* /16/ have also reported that the condensation products derived from the aromatic amines and carbonyl compounds give better inhibition than those derived from ethylene diamine and carbonyls. Thus the order of inhibition efficiencies based on the molecular structure of the compounds may be represented as below.

TBOAD>DBOAD>BMOAT>BOAH>MOAT>OAH

The better performance of compounds (4-9) in 1N HCl than in 1N H_2SO_4 can be explained by the fact that the chloride ions, being less hydrated than sulphate ions, are preferentially adsorbed on the metal surface thereby creating an excess negative charge towards the solution phase which favours synergistic adsorption of protonated inhibitors on the metal surface /17,18/.

Figure 2(b-d) shows the influence of acid concentration, temperature and immersion time on the inhibition efficiency of PTAT, PTAB and POAB. It is seen that an increase of acid concentration from 1N to 3N does not cause any significant change in IE values. However IE for all the compounds decreased in 5N HCl due to an increase in aggressivity of HCl. The IE of these compounds increases from 40-60°C but above 60°C IE decreases due to the desorption of inhibitors from the metal surface. The IE of all these

Table 3
Inhibition efficiencies and corrosion rates for different concentrations of macrocyclic compounds in 1N HCl and 1N H_2SO_4 from weight loss measurements at 35°C for 3 hours.

Inhibitor Concentration (ppm)	1N HCl		1N H_2SO_4	
	IE (%)	CR (mmpy)	IE (%)	CR (mmpy)
No Inhibitor	–	12.39	–	19.13
TBOAD				
100	78.3	2.69	77.4	4.31
200	82.0	2.22	81.3	3.57
300	86.1	1.71	82.3	3.38
400	90.3	1.20	83.0	3.25
500	93.6	0.78	84.9	2.87
1000	96.3	0.46	88.7	2.55
DBOAD				
100	72.7	3.38	77.3	5.10
200	77.9	2.73	77.7	4.22
300	82.0	2.22	81.3	3.57
400	87.3	1.57	82.3	3.38
500	89.1	1.34	83.5	2.04
1000	94.0	0.74	87.1	2.46
BMOAT				
100	64.4	4.41	30.5	13.28
200	77.5	2.78	37.1	11.23
300	82.7	2.13	40.2	11.82
400	85.0	1.85	50.0	9.40
500	90.2	1.20	51.4	9.13
1000	98.5	0.18	65.2	6.52
MOAT				
100	48.1	7.19	20.3	15.23
200	62.9	4.59	28.3	13.69
300	64.7	4.36	31.1	13.14
400	68.1	3.94	40.5	11.37
500	71.9	3.48	42.4	11.00
1000	84.6	1.90	54.1	8.77
BOAH				
100	56.1	5.43	23.0	14.72
200	66.2	4.17	32.7	12.64
300	70.7	3.62	35.9	12.25
400	74.1	3.20	41.2	11.23
500	74.9	3.05	46.3	10.26
1000	88.0	1.46	59.7	7.70
OAH				
100	47.5	6.50	10.9	17.04
200	53.1	5.80	18.6	15.55
300	63.3	4.55	21.1	15.04
400	68.5	3.90	25.2	14.30
500	68.9	3.85	27.1	13.93
1000	83.5	2.04	31.3	13.14

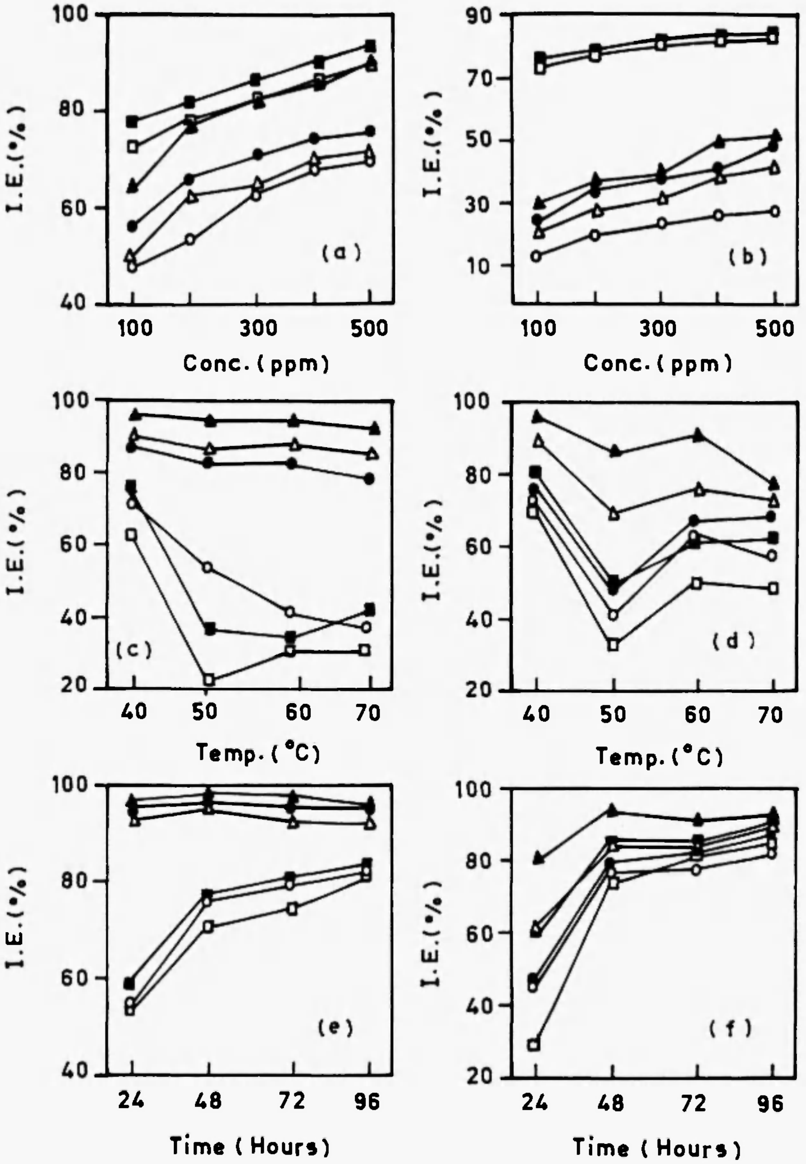


Fig. 3: Variation of inhibition efficiency with:

1. Inhibitor concentration (ppm) (a) in 1N HCl (b) in 1N H_2SO_4
2. Temp. (°C) (c) in 1N HCl (d) in 1N H_2SO_4
3. Immersion time (hours) (e) in 1N HCl (f) in 1N H_2SO_4

■ TBOAD, □ BDOAD, ▲BMOAT, △MOAT, ● BOAH, ○ OAH compounds increases with the increase in immersion time which may be attributed to the formation of a barrier film which prevents the attack of acid on metal surface.

Figure 3(c-f) show the variation of IE of TBOAD, DBOAD, BMOAT, MOAT, BOAH and OAH with temperature and immersion time in 1N HCl and 1N H_2SO_4. In both the acids it is found that IE decreases with the increase in temperature, indicating that the inhibitor film formed on the metal surface is less protective in nature at high temperature (Figure 3c-d). The desorption of the inhibitor molecules from the metal surface occurs at a faster rate at high temperature /19/. Figure 3(e-f) shows the variation of IE with immersion time in both acids. The IE of these compounds increases with increase in immersion time.

Synergism:

The values of IE obtained for macrocyclic compounds in combination with KI in acid solutions are given in Tables 4 and 5. The results show that

Table 4

Inhibition efficiencies of macrocyclic compounds obtained from weight loss measurements in the absence and presence of KI.

Inhi. Conc.	KI Conc.	IE (%)		
(PPM)	(%)	PTAT	PTAB	POAB
1 N HCl				
100	--	74.50	64.00	61.30
100	0.02	82.60	79.60	76.40
300	–	79.50	76.80	74.30
300	0.02	85.60	80.90	78.40
3 N HCl				
200	--	79.50	54.00	53.00
200	0.05	86.70	74.90	70.30
500	--	87.70	66.30	67.70
500	0.05	90.80	76.70	78.70
5 N HCl				
500	–	52.20	32.60	30.00
500	0.10	76.40	60.90	57.80
1000	–	70.20	48.30	45.10
1000	0.10	80.60	66.00	60.00

Table 5

Inhibition efficiencies of macrocyclic compounds obtained from weight loss measurements in the absence and presence of KI.

1N HCl			1N H_2SO_4		
Inhl. Conc. (PPM)	KI Conc. (%)	IE (%)	Inhl. Conc. (PPM)	KI Conc. (%)	IE (%)
TBOAD					
200	–	82.02	300	–	82.28
200	0.02	92.90	300	0.03	97.10
400	–	90.26	500	–	84.95
400	0.02	97.00	500	0.03	99.80
DBDAD					
200	–	77.90	300	–	81.31
200	0.02	89.50	300	0.03	98.30
400	–	87.27	500	–	83.06
400	0.02	96.30	500	0.03	99.50
BMOAT					
300	–	82.77	400	–	50.00
300	0.02	97.38	400	0.03	98.30
400	–	85.02	500	–	51.46
400	0.02	98.88	500	0.03	99.27
MOAT					
300	–	64.79	400	–	40.53
300	0.02	95.88	400	0.03	83.90
400	–	68.16	500	–	42.48
400	0.02	98.50	500	0.03	87.86
BOAH					
300	–	70.78	400	–	41.26
300	0.02	97.75	400	0.03	96.36
400	–	74.16	500	–	46.36
400	0.02	99.25	500	0.03	98.54
OAH					
300	–	63.30	400	–	25.74
300	0.02	70.64	400	0.03	78.88
400	–	68.54	500	–	27.18
400	0.02	77.52	500	0.03	91.75

IE increases with the addition of iodide ions for all of the compounds in the range of 10-40%. This was a result of the synergistic effect /20/. The S_I values obtained for six macrocyclic compounds and KI were calculated using the Aramaki and Hackerman equation /21/ and found to be more than 1 (Table 6). This further confirmed the existence of synergism between macrocyclic compounds and KI. Similar synergistic effects have been reported in nitrogen containing compounds with KI in acid media /22,23/.

Table 6

Synergistic parameters S_I for various concentrations of macrocyclic compounds in HCl and H_2SO_4 solutions.

Inhibitor	1N HCl		1N H_2SO_4	
	Inhl. Conc. (ppm)	S_I	Inhl. Conc. (ppm)	S_I
TBOAD	200 400	1.21 1.53	300 500	1.58 20.00
DBOAD	300 500	1.01 1.65	300 500	2.88 8.60
BMOAT	300 400	2.76 5.56	400 500	9.30 21.03
MOAT	300 400	3.56 8.83	400 500	1.17 1.50
BOAH	300 400	5.40 14.33	400 500	5.10 11.61
OAH	300 400	1.12 1.11	400 500	1.01 2.63

Adsorption Isotherm:

The plots of θ vs log C gave straight lines in all acid solutions for all macrocyclic compounds (Figure 4(a-c), Figure 5(a, b)). This showed that the adsorption of macrocyclic compounds on the mild steel surface in 1N -5N HCl and 1N H_2SO_4 obeyed Temkin's adsorption isotherm. This also clearly showed the corrosion inhibition by these compounds being a result of their adsorption on the metal surface.

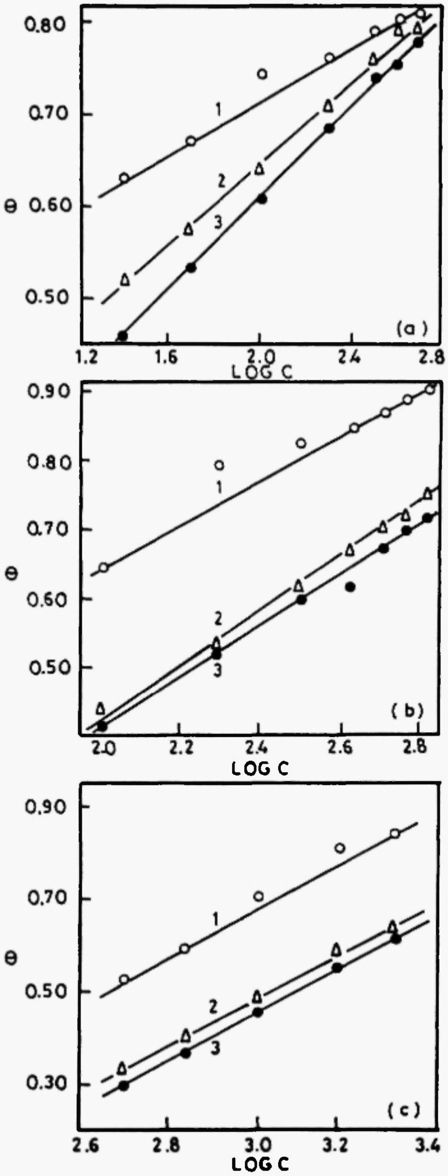


Fig. 4: Temkin's adsorption isotherm plots for mild steel in (a) 1N (b) 3N (c) 5N HCl containing different concentration of macrocyclic compounds:

1. PTAT 2. PTAB 3. POAB

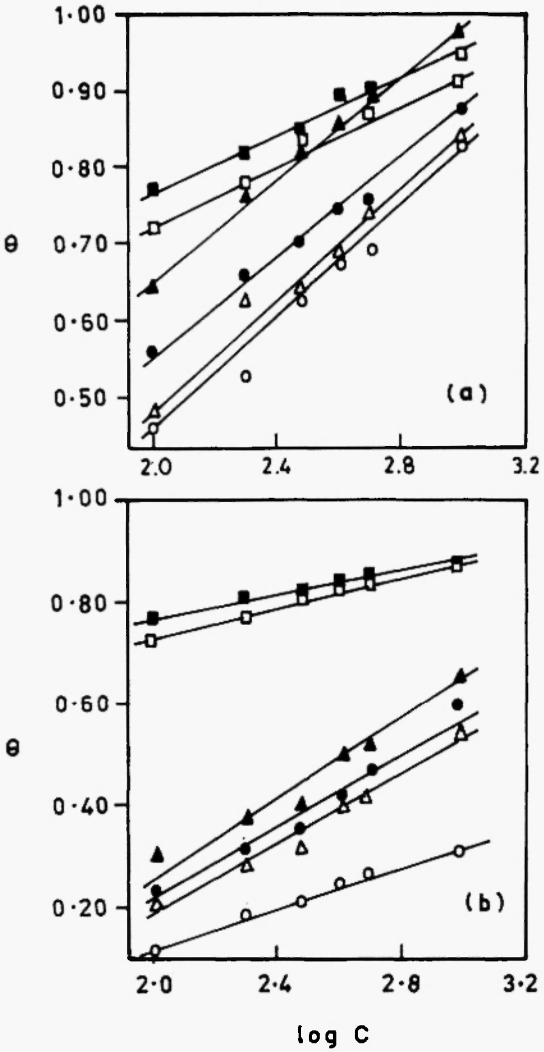


Fig. 5: Temkin's adsorption isotherm plots for mild steel in (a) 1N HCl (b) 1N H_2SO_4 containing different concentrations of macrocyclic compounds:
■ TBOAD, □ BDOAD, ▲BMOAT, △MOAT, ● BOAH, ○ OAH

Potentiodynamic Polarization Studies:

The anodic and cathodic polarization behavior of mild steel in the absence and presence of different concentrations of all macrocyclic compounds is shows in Fig 6(a-c) and Fig. 7(a-d). Various corrosion parameters obtained from the polarization curves such as corrosion current density (I_{corr}),

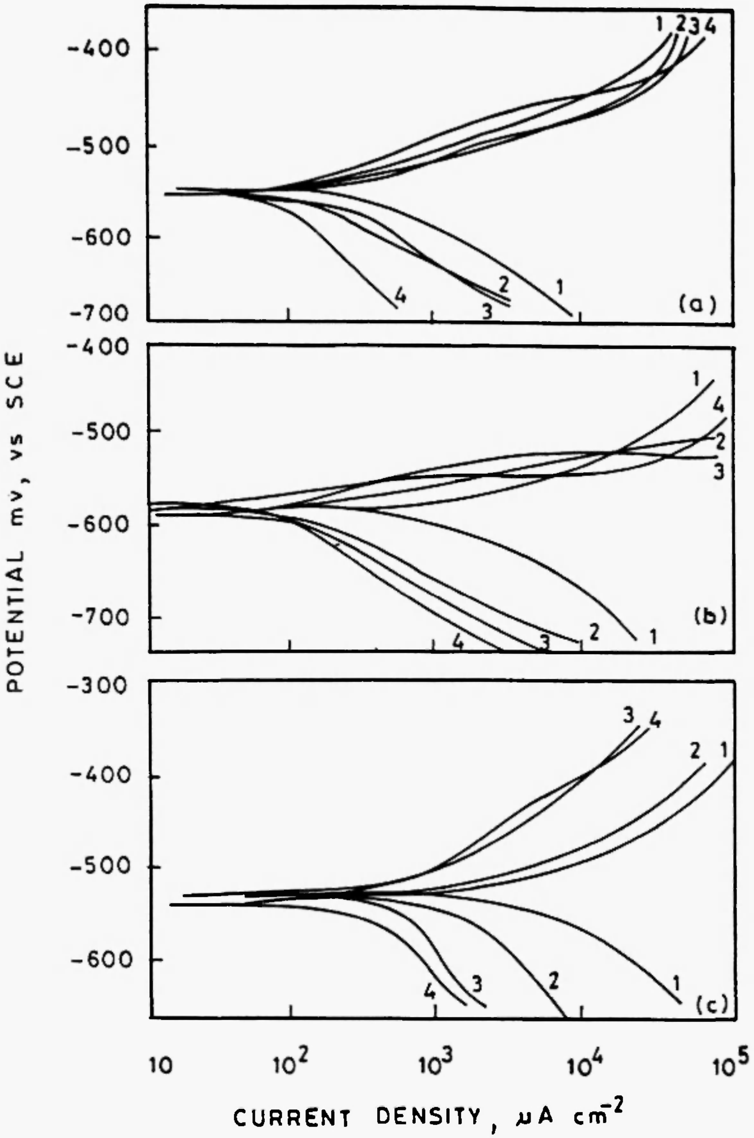


Fig. 6: Potentiodynamic polarization curves for mild steel in

(a) 1N HCl containing 500 ppm of macrocyclic compounds.

(b) 3N HCl containing 700 ppm of macrocyclic compounds.

(c) 5N HCl containing 1000 ppm of macrocyclic compounds.

1. Blank 2. POAB 3. PTAB 4. PTAT.

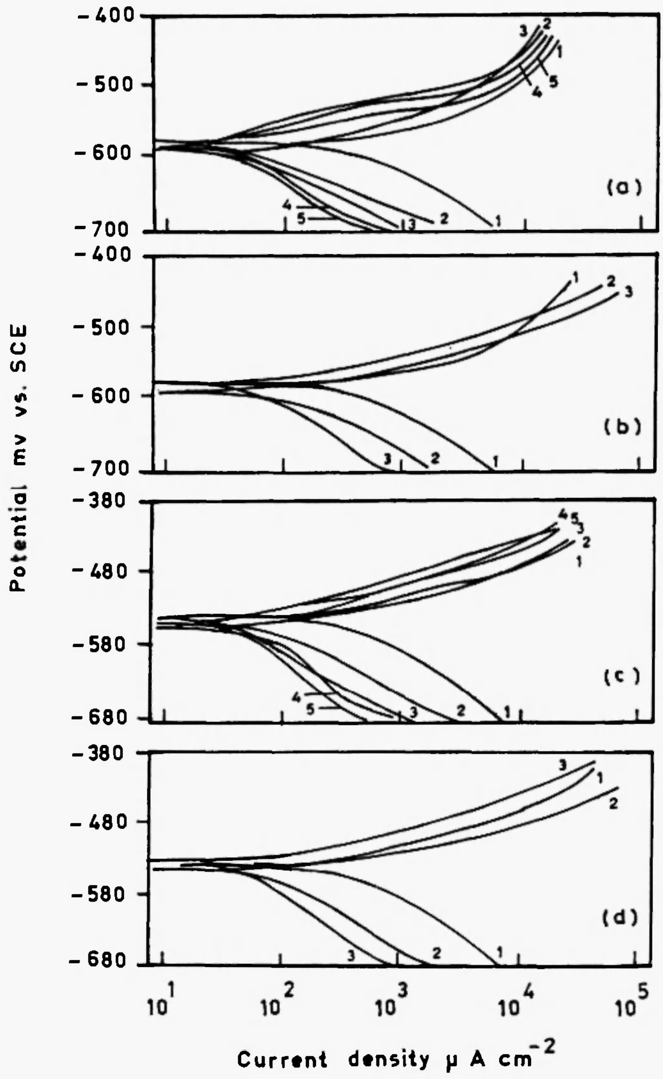


Fig. 7: Potentiodynamic polarization curves for mild steel in absence and presence of 1000 ppm of macrocyclic compounds:

(a) 1N H_2SO_4 : 1. Blank 2. OAH 3. BOAH 4. MOAT 5. BMOAT

(b) 1N H_2SO_4 : 1. Blank 2. DBOAD 3. TBOAD

(c) 1N HCl : 1. Blank 2. OAH 3. BOAH 4. MOAT 5. BMOAT

(d) 1N HCl : 1. Blank 2. DBOAD 3. TBOAD

corrosion potential (E_{corr}) and inhibition efficiency of all compounds are given in Tables 7 and 8. These results show that all the compounds bring down I_{corr} value in all concentrations but maximum decrease in I_{corr} value is obtained at 500, 700 and 2000 ppm in 1N, 3N and 5N HCl respectively for PTAT, PTAB and POAB, whereas TBOAD, DBOAD, BMOAT, MOAT, BOAH and OAH has shown maximum decrease in I_{corr} value at 1000 ppm concentration in 1N HCl and 1N H_2SO_4.

Table 7

Electrochemical polarization parameters for corrosion of mild steel in 1N, 3N, and 5N HCl in the presence of different concentrations of macrocyclic compounds at 35°C ± 2°C.

Inhibitor Concentration (ppm)	PTAT			PTAB			POAB		
	I_{corr} (pAcm^{-2})	E_{corr} (mV)	IE (%)	I_{corr} (μAcm^{-2})	E_{corr} (mV)	IE (%)	I_{corr} (μAcm^{-2})	E_{corr} (mV)	IE (%)
1N HCl	350	-554	-	350	-554	-	350	-554	-
50	86	-550	75.4	140	-564	60.0	190	-564	45.7
100	78	-552	77.5	110	-560	68.5	160	-552	54.2
300	82	-556	76.5	120	-562	65.7	150	-562	57.1
400	76	-558	78.2	100	-552	71.4	135	-550	61.4
500	74	-560	78.8	90	-562	72.2	120	-560	65.7
3N HCl	1200	-568	-	1200	-568	-	1200	-568	-
100	374	-574	68.8	467	-567	61.1	529	-566	55.9
300	346	-578	71.2	436	-566	63.7	462	-570	61.5
500	176	-562	85.3	360	-574	70.0	387	-574	67.8
700	163	-565	86.4	263	-573	78.1	356	-578	70.3
5N HCl	4000	520	-	4000	-520	-	4000	-520	-
500	720	-528	82.0	1000	-524	75.0	1800	-524	55.0
700	550	-536	86.2	920	-524	77.0	1200	-530	70.0
1000	340	-530	91.5	640	-526	84.0	1100	-226	72.5
2000	330	-538	91.7	560	-524	86.0	1000	-522	75.0
700+KI	420	-540	89.5	460	-536	88.5	480	-520	88.0
1000+KI	328	-542	91.80	400	-540	90.0	440	-522	89.0

E_{corr} values obtained for PTAT, PTAB and POAB in 1-5 N HCl do not show a significant shift, thereby showing the mixed nature of inhibitors (Fig. 6(a-c)).The macrocyclic compounds BMOAT, MOAT, BOAH and OAH exhibited mixed behavior in 1N HCl and predominantly cathodic in 1N H_2SO_4 (Fig. 7(a,c)), whereas TBOAD and DBOAD has shown mixed behavior in both acids (Fig. 7 (b, d)). All of these compounds also showed synergistic effect in presence of KI (Tables 7and 8).

Table 8

Electrochemical polarization parameters for corrosion of mild steel in 1N HCl and 1N H_2SO_4 in the presence of different concentrations of macrocyclic compounds at 35°C.

	1N HCl				1N H_2SO_4		
Inhibitor Concentration (ppm)	**E_{corr} mv**	**I_{corr} (μAcm^{-2})**	**IE (%)**	**Inhibitor Concentration (ppm)**	**E_{corr} mv**	**I_{corr} (μAcm^{-2})**	**IE (%)**
No Inhibitor	-554	350	-	**No Inhibitor**	-580	380	-
TBOAD				**TBOAD**			
200	-562	160	54.3	200	-592	120	68.4
400	-560	100	71.4	500	-590	82	78.4
1000	-554	72	79.4	1000	-594	56	85.3
400+KI	-552	66	81.1	500+KI	-588	66	82.6
DBOAD				**DBOAD**			
200	-566	180	48.6	200	-580	120	68.4
400	-568	120	65.7	500	-584	82	78.4
1000	-562	96	72.6	1000	-578	52	86.3
400+KI	-560	98	72.0	500+KI	-586	58	84.7
BMOAT				**BMOAT**			
100	-546	180	48.6	100	-596	180	52.6
400	-532	130	62.9	500	-598	120	68.4
1000	-526	74	78.9	1000	-572	55	85.5
400+KI	-534	58	83.4	500+KI	-584	37	90.3
MOAT				**MOAT**			
100	-544	190	45.7	100	-584	220	42.1
400	-530	120	65.7	500	-562	140	63.2
1000	-522	88	74.9	1000	-544	94	75.3
400+KI	-534	60	82.9	500+KI	-548	68	82.1
BOAH				**BOAH**			
100	-548	170	51.4	100	-582	150	60.5
400	-544	120	65.7	500	-586	130	65.8
1000	-530	80	77.1	1000	-584	76	80.0
400+KI	-528	62	82.3	500+KI	-598	55	85.5
OAH				**OAH**			
100	-548	200	42.9	100	-582	200	47.4
400	-546	130	62.9	500	-586	180	52.6
1000	-520	110	68.6	1000	-576	120	68.4
400+KI	-522	70	80.0	500+KI	-600	70	81.6

Electrochemical Impedance Studies:

Three macrocyclic compounds (PTAT, PTAB and POAB) have been investigated by ac impedance studies Nyquist plots obtained from the impedance studies in 1N HCl containing 500 ppm of inhibitors are shown in Figure 8(a-c). Various parameters such as charge transfer resistance (R_t),

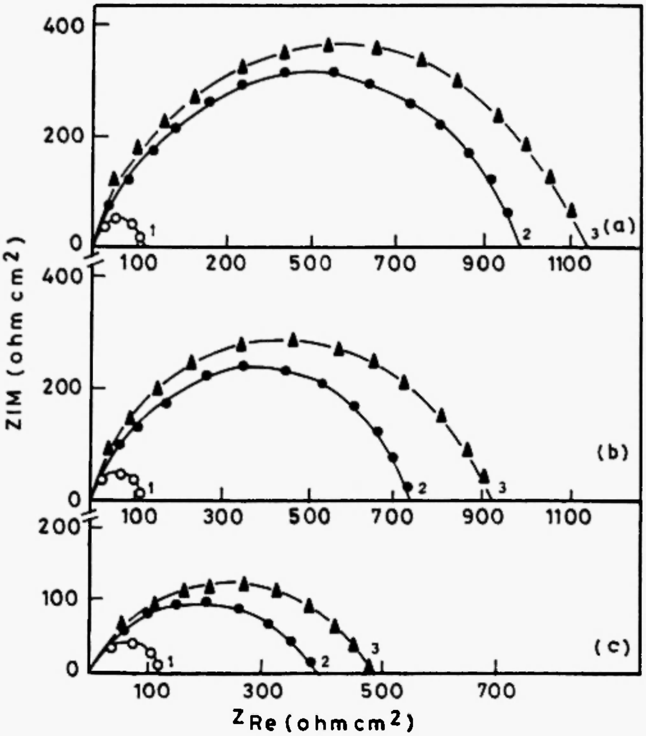


Fig. 8: Nyquist plots for mild steel in 1N HCl in absence and presence of different concentrations of macrocyclic compounds:
(a). PTAT (b). PTAB (c). POAB 1. Blank 2. 300ppm 3. 500 ppm

double layer capacitance (C_{dl}), corrosion current density (I_{corr}) and IE are given in Table 9. R_t values were calculated from the difference in impedance at lower and higher frequencies as suggested by Tsuru and Haruyama /24/. I_{corr} values were calculated by the Stern - Geary equation, C_{dl} values were calculated from the frequency at which the imaginary component of impedance was maximum (Z_{im} max) using the relation:

$$C_{dl} = \frac{1}{2\pi f_{max}} \times \frac{1}{R_t}$$

where f_{max} = Frequency at which the imaginary component of impedance is maximum.

Table 9
Impedance data of mild steel in 1N HCl containing different concentrations of macrocyclic compounds

SYSTEM	Inhi. Conc. (ppm)	R_t (Ω cm^2)	C_{dl} (μF cm^{-2})	I_{corr} (μ A cm^{-2})	I E (%)
1 N HCl	--	115	12832	155.2	--
PTAT	300	969	1623	18.5	88.13
	500	1156	1464	13.6	90.06
PTAB	300	746	2089	23.3	84.59
	500	962	1758	18.5	88.10
POAB	300	407	4338	43.8	71.79
	500	500	3384	35.6	77.10

The results clearly show that I_{corr} and C_{dl} values are less for inhibited systems as compared to those for uninhibited system and R_t values are higher for inhibited systems. These observations suggest that macrocyclic compounds inhibit corrosion by getting adsorbed on the metal surface, which increases the impedance (resistance) of the metal surface which in turn decreases I_{corr} as well as C_{dl} values.

Hydrogen Permeation Studies:

Macrocyclic compounds (PTAT and PTAB) have been investigated by hydrogen permeation study to evaluate the effect of inhibitors on the reduction of hydrogen permeation.

The permeation current vs time curves for mild steel in 1N HCl in the absence and presence of inhibitors are shown in Figure-9. Both of the compounds considerably reduce the hydrogen permeation current which may be attributed to the adsorption of these compounds on mild steel surface which prevents the entry of hydrogen into the metal.

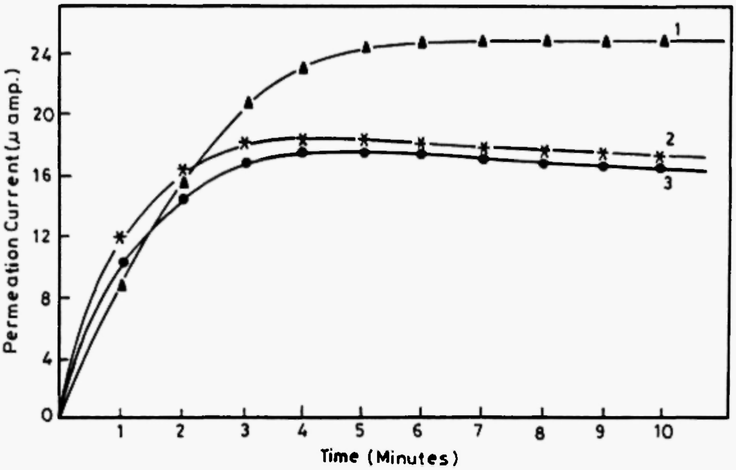


Fig. 9: Hydrogen permeation curves for mild steel in 1N HCl in absence and presence of 500 ppm of macrocyclic inhibitors:-
1. Blank 2. PTAB 3. PTAT

Auger Electron Spectroscopic Studies:

The auger electron spectra for polished mild steel surface and mild steel exposed to a solution of PTAT and PTAT + KI are shown in Figure 10(a-c). The appearance of peaks at 378 and 152 ev confirms the adsorption of PTAT on mild steel surface through nitrogen and sulphur atoms; similarly the appearance of peaks at 511, 379 and 152 ev proves the presence of iodine, nitrogen and sulphur atoms respectively on mild steel inhibited with PTAT in the presence of KI.

CONCLUSIONS

The main conclusions drawn from all these studies of macrocyclic compounds are:-

1. All the investigated macrocyclic compounds show good inhibition efficiency in acid solutions.
2. The IE of all macrocyclic compounds increases with increase in inhibitor concentration and immersion period whereas it decreases with the increase of temperature and acid concentration.

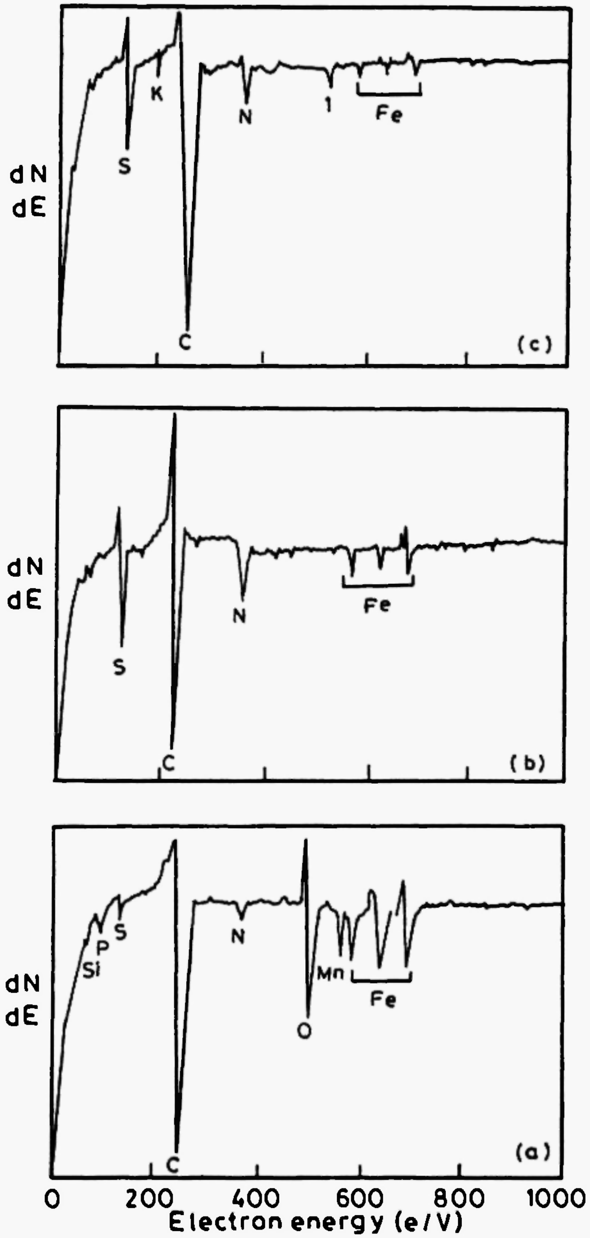


Fig. 10: Auger electron spectrum for:-
(a) polished mild steel surface
(b) mild steel exposed to PTAT
(c) mild steel exposed to PTAT + KI

3. The IE of all compounds follows the order: PTAT>PTAB>POAB in 1N-5N HCl and TBOAD>DBOAD>BMOAT>MOAH>MOAT>OAH in 1N HCl and 1N H_2SO_4.
4. The IE of all the tested compounds increased on the addition of KI due to synergistic effect.
5. The adsorption of all the compounds on mild steel surface from the acidic solutions obeys Temkin's adsorption isotherm.
6. PTAT, PTAB, POAB behave as mixed inhibitors in 1N-5N HCl whereas BMOAT, MOAT, BOAH, OAH behave as mixed inhibitors in HCl and predominantly cathodic in 1N H_2SO_4. TBOAD and DBOAD have shown mixed behavior in both 1N HCl and 1N H_2SO_4.
7. PTAT, PTAB and POAB increase R_t values and decrease I_{corr} and C_{dl} values in 1N HCl.
8. PTAT and PTAB reduce hydrogen permeation current considerably in 1N HCl.
9. AES study confirms the adsorption of macrocyclic compounds through sulphur and nitrogen atoms.

REFERENCES

1. M. Zemer and M. Gouterman, *Theor. Chem. Acta*, **4**, 44 (1966).
2. A. Show and N. Jarvis, *J. Am. Chem. Soc.*, **106**, 4706 (1984).
3. F.R. Longo, J.J. Deluccia and V.S. Agrawala "Corrosion prevention by organic inhibitors", *Proc. 6th Europ. Symp. Corrosion Inhibitors,* Univ. of Ferrara, Italy, 1985; p. 155.
4. V.S. Agrawala, "New approach in corrosion inhibition", *Proc. Int. Cong. Metallic Corrosion,* Toronto, Canada, 1984; 1, p. 380.
5. S. Hettiarachchi, Y.W. Chan, R.B. Wilson, Jr. and V.S. Agarwala, *Corrosion*, **45**, 30 (1989).
6. V.N.S. Pillai, J. Thomas and P.S. HariKumar, *Ind. J. Chem. Technol,* **2**, 93 (1995).
7. Jaya Rawat, "Physico Chemical Studies on Some Metallic Corrosion Inhibitors" Ph.D. Thesis, 1998; pp. 70-72.
8. P.B. Mathur and T. Vasudevan, *Corrosion*, **38**. 17 (1982).
9. Standard Practice for Laboratory Immersion Corrosion Testing of Metals G 31-72, ASTM (1990).

10. M.A.V. Devananthan and Z. Stachurski, *Proc. Roy. Soc. A*, **270**, 90 (1962).
11. K.N. Srinivasan, M. Selvan and S.V.K. Iyer, *J. Appl. Electrochem.*, **23**, 318 (1993).
12. F. Zucchi and G. Trabanelli, "Influence of some nitrogen containing heterocyclic compounds on steel corrosion in hydrochloric acid", *Proc. 7th Europ. Symp. Corros. Inhibitors.* Ann. Univ. Ferrara, N.S., Vol. 5. Suppl. 9, 1990; p. 339.
13. M.A. Quraishi, J. Rawat and M. Ajmal, *Corrosion*, **54** (12), 996 (1998).
14. M. Ajmal, J. Rawat and M.A. Quraishi, *Bulletin of Electrochemistry*, **14** (6-7), 199 (1998).
15. M. Ajmal, J.Rawat and M.A. Quraishi, *Anticorrosion Methods and Materials*, **45** (6), 419 (1998).
16. M.N. Desai, M.B. Desai, C.B. Shah and S.M. Desai "Schiffs bases as inhibitors for mild steel in hydrochloric acid solutions", *Corrosion Science*, **26**, 827 (1986).
17. M.A. Quraishi, M.A.W. Khan, M. Ajmal, S. Muralidharan and S. Angappan, *Portugaliae Electrochimica Acta*, **13**, 63 (1995).
18. S.L. Granese, B.M. Rosales, C. Oviedo and J.O. Zerbino, *Corrosion Science*, **33** (9), 1439 (1992).
19. I.N. Putilova, S.A.Balezin and U.P. Baranki, *Metallic Corrosion Inhibitors*, Pergamon Press, New York, NY, 1960; p. 31.
20. R.T. Foley, *Corrosion*, **26**, 58 (1970).
21. K. Aramaki and N. Hackerman, *J. Electrochem Soc.*, **116**, 568 (1969).
22. S.S. Azim and S.V. Iyer "Synergistic effect of dicyclohexylamine with halide ions on the corrosion of mild steel in sulphuric acid medium", *Proc. 10th Int. Cong. Metall. Corros.* (Madras, India) 1987; p. 2.935.
23. M. Ajmal, J. Rawat and M.A. Quraishi, *J. The Electrochemical Society of India*, **49**, 70 (1999).
24. T. Tsuru and S. Haruyama, *Bosohoku Gijutsu, J. Jpn. Soc. Corros. Eng.*, **27**, 449, 573 (1978).