CORROSION SCIENCE AND ENGINEERING

CORROSION INHIBITORS FOR ZINC IN ORGANIC AND INORGANIC ACIDS

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Some alkaloids of vegetable origin namely narcotine, papaverine, brucine, strychnine, cinchonidine, quinidine and ephedrine were examined by weight loss and polarization measurements with regard to their inhibitive effect on the corrosion of zinc in 1M solutions of tartaric, citric, acetic, propionic, mono-, di- and trichloracetic acids. In the hydroxy acids the opium and the nuxvomica alkaloids give inhibition efficiency ranging from 58 to 82%, papaverine leading the others. In the mono carboxylic acids the performance of all the alkaloids is poor except that of papaverine. In chloracetic acids narcotine, papaverine and brucine give inhibition efficiency of 70% or more at the higher concentrations only in monochloracetic acid. The polarization experiments of zinc in the systems giving more than 50% inhibition efficiency have also been carried out.

The effect of cetyl trimethyl ammonium bromide (CTAB) and hexadecyl pyridinium chloride (HDPC) on the corrosion of zinc in hydrochloric and sulphuric acids has also been investigated. It has been observed that the performance of HDPC is better (I.E. 99.0%) than that of CTAB in both the media and this has been attributed to the presence of a pyridine ring in the former. From polarization experiments it is concluded that the inhibitive action of HDPC is under cathodic control as evidenced by appreciable cathodic polarization, whereas that of CTAB is under mixed control. The results are discussed.

Key Words : Zinc, inhibitors, alkaloids, weight loss, polarization, efficiency

INTRODUCTION

Corrosion inhibitors for zinc

Zinc is an industrially important and useful metal finding wide Zapplication in areas of battery technology, as a sacrificial anode in cathodic protection systems, in the preparation of metallic coatings and so on. Although the dissolution of the metal is a requirement in its function as an anode, its corrosion is undesirable in the case of its use in metallic coatings and other applications. Incorporation of inhibitive compounds viz inorganic and organic chemicals and sometimes their mixtures is one of the known methods to combat the corrosion of metals in closed systems.

Quaternary ammonium compounds

On account of the availability of electrons around nitrogen, oxygen, sulphur and phosphorus atoms, these elements react with the protons of the aqueous medium to form positively charged onium compounds of practical importance. The compounds derived from nitrogen viz quaternary ammonium compounds, are employed as corrosion inhibitors, microbiocides, and in other cleaning applications. The performance of these compounds as corrosion inhibitors is dependent on the nature of the substituent groups. The biocidal action of quaternaries is very effective against Grampositive bacteria, fungi and protozoa, and less effective on bacterial and fungal spores. The mechanism of action of these compounds is attributed to protein denaturation, enzyme inhibition and disruption of the cell membranes. The quaternary ammonium compounds are incorporated as members in cooling water inhibitor formulations in heat exchangers to maintain the heat transfer surfaces clean and thereby to promote efficient heat transfer.

and citric acids are used as cleaning agents for ferrous and nonferrous items in composite equipments like engine and automobile cooling systems. It is desirable to minimize metal loss during cleaning operations by the incorporation of corrosion inhibitors in the cleaning solutions. In this direction some reports have been published on the performance of alkaloids on the corrosion of steel in sulphuric [1] and hydrochloric acids [2], aluminium in acid and alkaline solutions [3] and zinc in sulphuric and hydrochloric [4,5]acids. The inhibitive performance of alkaloids has also been reported [6] for the corrosion of steel and copper components in sodium chloride solutions.

The organic compounds containing oxygen, sulphur and nitrogen atoms are of interest in corrosion inhibition. It has been reported that these molecules form a type of chemical bond with the metal atoms and bring about corrosion inhibition. The nitrogen containing organic compounds e.g. alkyl and aryl amines in aqueous media form positively charged ions of the quaternary ammonium type and are attracted toward the metal surface by electrostatic interaction. The long chain n-alkyl quaternary ammonium compounds form surface active cations and are adsorbed on the metal surfaces to bring about corrosion inhibition and the effects of CTAB and cetyl pyridinium bromide have been investigated with regard to the corrosion of steel in acids [7].

This work is an extension of the study on the effect of some alkaloids of plant origin on the corrosion of zinc in 1M solutions of tartaric, citric, acetic, propionic and chloracetic acids. The performance of CTAB and HDPC on the corrosion of zinc in hydrochloric and sulphuric acids is also examined and included for comparison.

EXPERIMENTAL

	Materials
Objective	Metal specimens
Apart from mineral acids many organic acids like gluconic, tartaric	Rectangular specimens of electrolytically pure zinc of 5 cm x 2 cm x

0.15 cm size were employed for determination of the corrosion rate. Circular specimens of 1 cm dia with a stem of 8 cms were used for polarization experiments. The specimens were polished with Ronuk's emery compound and degreased with trichloroethylene.

Chemicals

All the alkaloids, CTAB, HDPC and the organic acids used were of L.R. grade. Sulphuric and hydrochloric acids employed were of A.R. quality. All the solutions were prepared with distilled water.

Procedure

Determination of corrosion inhibition

Three rectangular specimens, weighed after cleaning and degreasing with trichloroethylene were suspended by means of glass hooks in 250 ml of the corrosive solution for a known duration. At the end of this period the metal specimens were taken out, washed thoroughly under running tap water and then cleaned in chromic acid solution |8|. The specimens were again washed with tap water and distilled water. They were then dried and weighed. Taking the average of the weight losses by the specimens, the inhibition efficiency was calculated according to the formula

Inhibition efficiency (%) =
$$\frac{(W - W_1)}{W} \times 100$$

where W and W_1 are the weight losses without and with the added substance in the particular acid solution.

Polarization experiments

The polarization experiments were carried out using circular specimens. The area of the electrode exposed to the electrolyte solution (250 ml) was 0.785 cm². Platinized platinum sheet of 6.25 cm² area was employed as the auxiliary electrode. The cell had a separate compartment for the reference electrode. During the course of the experiment the contents of the cell were kept stirred by means of a magnetic stirrer. After measuring the steady state potential, the polarization was carried out by passing known values of current drawn from a constant direct current source. The potentials of the test electrode were measured by means of vacuum tube voltmeter (D.C. micro-voltmeter G.M. 6020). The experiments were carried out at 23 \pm 2°C in duplicate.

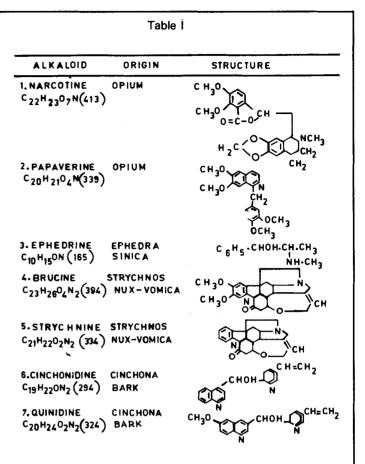
RESULTS AND DISCUSSION

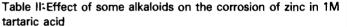
Alkaloids

Corrosion inhibition

The details regarding the structures, occurrence, molecular formulae and molecular weights of the alkaloids are shown in Table - I. The influence of these alkaloids on the corrosion of zinc in 1M tartaric acid is brought out in Table II. Of these alkaloids, only narcotine, papaverine, brucine and strychnine show tangible performance and the values of inhibition efficiency at the lowest concentration of the inhibitor follow the order

Narcotine (45%)	<	Strychnine (60%)	< Brucine (66%)
			Papaverine (75%)





(Duration 5 hrs.)

Alkaloid	Inhibition efficiency (%) at						
	Concentration of the alkaloid (M)						
	2.4×10^{-4}	1.2×10^{-3}	2.4×10^{-3}	4.8×10^{-3}			
1. Narcotine	45	46	43	53			
2. Papaverine	75	75	87	84			
3. Ephedrine	24	6	- 1	<u> </u>			
4. Brucine	66	75	68	75			
5. Strychnine	60	64	59	58			
6. Cinchonidine	—19	-13	7	20			
7. Quinidine	-13	2	26	36			

In this medium, papaverine shows better performance than narcotine and these two belong to the group of isoquinoline alkaloids. Of these two opium alkaloids, papaverine having the lower molecular weight shows better inhibition than narcotine. Therefore, adsorption apart, the inhibition is to be understood in terms of orientation in a preferred manner rather than merely on the basis of the size of the molecule. With these alkaloids, the values of inhibition efficiency do not increase significantly with increase in concentration. The inhibition efficiency of the other alkaloids is either very poor, or they even accelerate corrosion at the lower concentrations.

The inhibition efficiency data obtained with these alkaloids in 1M citric acid are shown in Table III.

 Table III: Effect of some alkaloids on the corrosion of zinc in 1M

 citric acid

 (Duration 5 hrs.)

	Inhibition efficiency (%) at					
	Concentration of the alkaloid (M)					
Alkaloid	2.4x10 ⁻⁴	1.2x10-3	2.4x10-3	4.8x10-3		
1. Narcotine	54	71	73	77		
2. Papaverine	69	82	82	82		
3. Ephedrine	28	24	43	46		
4. Brucine	71	71	74	81		
5. Strychnine	68	70	62	63		
6. Cinchonidine	49	34	24	-18		
7. Quinidine		25	-20	-13		

It is to be noted that the performance of ephedrine is considerably better in this medium than in tartaric acid. Perhaps this may be due to the formation of an insoluble complex of zinc with ephedrine and citric acid which has got inhibitive properties. Except cinchonidine and quinidine, the other alkaloids show inhibitive performance for the corrosion of zinc in this medium and the values of inhibition efficiency follow the order:

Ephedrine < Strychnine < Brucine (at higher concentrations) \simeq Narcotine < Papaverine

The inhibitive effects of the compounds brucine, papaverine and narcotine are comparable. Further it is to be seen from the results of Tables II and III that the performance of brucine is greater in both the media than that of strychnine. Brucine is a dimethoxy derivative of strychnine. The inhibitive efficiencies of brucine and strychnine are more or less comparable in these media. Further, it is to be noted that the performance of narcotine is better in citric acid than in tartaric acid and papaverine maintaining the same degree of effectiveness.

In 1M acetic acid, except papaverine, all these compounds accelerate corrosion appreciably and the inhibition efficiency of papaverine is 82% at the highest concentration (Table IV). In 1M propionic acid (Table V) also only papaverine shows the inhibitive effect (I.E. \simeq 50%) and the values of inhibition efficiency got with other alkaloids are low.

Cinchonidine and quinidine which were very corrosive in acetic acid do not accelerate corrosion to that extent in propionic acid. Ephedrine is more effective in propionic acid than in acetic acid and again brucine is better than strychnine in these media also. And narcotine is more corrosive in acetic acid than in propionic acid. Table IV: Effect of some alkaloids on the corrosion of zinc in 1M acetic acid (Duration 48 hrs.)

Alkaloid	I	nhibition e	fficiency (%	o) at	
	Concentration of the alkaloid (M)				
	2.4x10-4	1.2x10-3	2.4x10-3	4.8x10-3	
1. Narcotine	2	— 52	— 53	—105	
2. Papaverine	49	75	76	82	
3. Ephedrine	3	8	8	9	
4. Brucine	14	0	6	— 12	
5. Strychnine	61		251	251	
6. Cinchonidine	69	-103	— 12	- 96	
7. Quinidine	61	97	-100	-102	

Table V: Effect of some alkaloids on the corrosion of zinc in 1M propionic acid

(Duration 6 days)

Alkaloid	Inhibition efficiency (%) at						
	Con	Concentration of the alkaloid (M)					
	2.4x10-4	1.2x10 ⁻³	2.4x10-3	4.8x10 ⁻³			
1. Narcotine	- 7	- 4	4	14			
2. Papaverine	37	40	55	45			
3. Ephedrine	28	22	31	40			
4. Brucine	37	29	20	10			
5. Strychnine	— 5	- 5	6	10			
6. Cinchonidine		16	22	23			
7. Quinidine	—23	10	14	— 1			

The effect of these alkaloids on the corrosion of zinc in 1M solutions of chloracetic acids is brought out in Tables VI to VIII.

Table VI: Effect of some alkaloids on the corrosion of zinc in 1M chloracetic acid

(Duration 5 hrs.)

Alkaloid	Inhibition efficiency (%) at Concentration of the alkaloid (M)					
	1. Narcotine	36	68	84	89	
2. Papaverine	84	. 94	96	97		
3. Ephedrine	- 9	6	— 2	-13		
4. Brucine	25	41	70	74		
5. Strychnine	11	23	33	47		
6. Cinchonidine	-12	13	37	48		
7. Quinidine	12	32	46	51		

Table VII: Effect of some alkaloids on the corrosion of zinc in 1M dichloracetic acid (Duration 30 minutes)

Alkaloid	Inhibition efficiency (%) at					
	Concentration of the alkaloid (M)					
	2.4x10-4	1.2×10^{-3}	2.4x10-3	4.8x10-3		
1. Narcotine	17	20	23	13		
2. Papaverine	25	35	37	40		
3. Ephedrine	9	0	5	5		
4. Brucine	27	35	39	43		
5. Strychnine	11	24	29	33		
6. Cinchonidine	30	33	40	49		
7. Quinidine	31	34	41	48		

Table VIII: Effect of some alkaloids on the corrosion of zinc in 1M trichloracetic acid

(Duration 1 hour)

Alkaloid	I	nhibition e	fficiency (%	o) at	
	Concentration of the alkaloid (M)				
		1.2x10-3 1/4 Satn.	2.4x10 ⁻³ ½ Satn.	4.8x10-3 Satd.	
1. Brucine	—1	8	- 7	- 2	
2. Strychnine	4	3	— 9	-14	
3. Papaverine*	—3	0	17	—13	
4. Ephedrine*	—5	—2	8	3	

* Concentration expressed in terms of saturation in view of apparent insolubility

For narcotine and papaverine in monochloracetic acid medium (Table VI) the inhibition efficiency increases with increase in concentration and papaverine shows the best performance (I.E. 97%). In this medium ephedrine is an accelerator of corrosion giving only negative values of inhibition efficiency. In the case of brucine and strychnine also inhibition of the corrosion of metal increases with increase in concentration and brucine is more effective than strychnine. Cinchonidine and quinidine show their inhibitive effect, though not very much, at higher concentrations. In a general way it may be pointed out that these alkaloidal compounds are more effective in monochloracetic acid than in acetic acid. This may be attributed to the more favoured adsorption of the organic compound by chlorine substitution in acetic acid.

Now coming to the dichloracetic acid (Table VII), it may be noted that this is the medium in which all the organic compounds show positive inhibition efficiencies, though the values may not be high. Papaverine which has been showing high degree of inhibition in other organic acids, is only poor in its effect in this medium (I.E. 40%). Cinchonidine and quinidine are effective to the extent of 48% and the inhibition efficiency values are comparable. And in trichloracetic acid (Table VIII) all the four alkaloids studied viz brucine, strychnine, papaverine and ephedrine only accelerate the corrosion of zinc.

The performance of the two promising alkaloids, namely papaverine and brucine in the carboxylic acids and in the chloracetic acids can also be examined with respect to the corrosivity or in other words the s^{*}-ength of the acids, as given below:

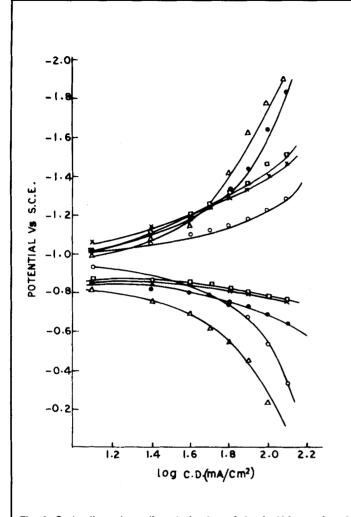
Prop	oionic cid	< Acetic acid <	Chloracetic acid <	Dichlorace	- Trichlorace- < tic acid
pK	4.88	4.76	2.86	1.29	0.65
pK _a Papave (I.E)	rine 45	82	97	40	Negative
Brucine (I.E.)	e 10	Negative	74	43	Negative

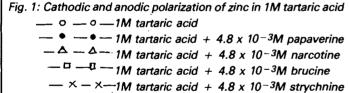
As indicated above the degree of ionization increases from propionic acid to trichloracetic acid. The inhibitive action of papaverine increases from 45% in propionic acid to a maximum of 97% in monochloracetic acid and then decreases and finally becomes an accelerator in trichloracetic acid. Therefore, it is apparent that two effects viz the action of inhibitor in reducing corrosion and the enhanced ionic dissociation promoting corrosion, as we go from propionic acid to trichloracetic acid are involved in the corrosion reaction. The inhibition efficiency of papaverine is maximum in monochloracetic acid. In di- and trichloracetic acids the degree of dissociation is comparatively greater providing greater concentration of depolarizers namely H+ ions and therefore the effectiveness of the inhibitor is reduced. Similarly, the performance of brucine is greater in monochloracetic acid, decreases in dichloracetic acid and it is an accelerator of corrosion in trichloracetic acid. It is to be noted that both in the case of papaverine and brucine, the values of inhibition efficiency do not progressively decrease with increase in strength of the acids. This may be attributed to a contribution made by acetic and monochloracetic acids to the inhibitive action of the two alkaloids by some compound formation.

Polarization

The polarization behaviour of the alkaloids which gave inhibition efficiency greater than 50% in 1M tartaric acid is shown in Fig.1. It can be seen that all these four alkaloids viz papaverine, narcotine, brucine and strychnine bring about significant cathodic polarization, although the polarization on the anodic side is less pronounced except in the case of narcotine. It is thus inferred that the inhibitive action of narcotine is under mixed control whereas the other alkaloids bring about inhibition mainly by cathodic polarization. In this connection it is also to be noted that the nitrogen containing organic compounds are mostly cathodic polarizers for the corrosion of metals in acid media [9].

In 1M citric acid good inhibitive performance is shown by narcotine, papaverine, ephedrine, brucine and strychnine and their effect on the polarization behaviour of zinc in this medium is shown in Figs. 2 and 2 (a). Ramakrishnaiah - Corrosion inhibitors for zinc in organic and inorganic acids





It is to be noted that the behaviour of papaverine and narcotine is quite significant in bringing about both cathodic and anodic polarization whereas in the case of ephedrine it is only the cathodic polarization that is well marked (Fig.2). Although both brucine and strychnine bring about anodic and cathodic polarizations, the effect of strychnine on anodic polarization is considerable (Fig.2a).

In acetic acid medium the effect of only papaverine was investigated on the polarization of zinc as this was the only compound giving good degree of inhibition and the results are shown in Fig.3. In this case also it is quite evident as to its effect on cathodic polarization and it acts as a cathodic inhibitor.

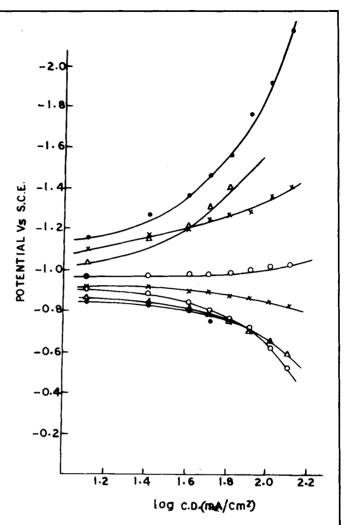


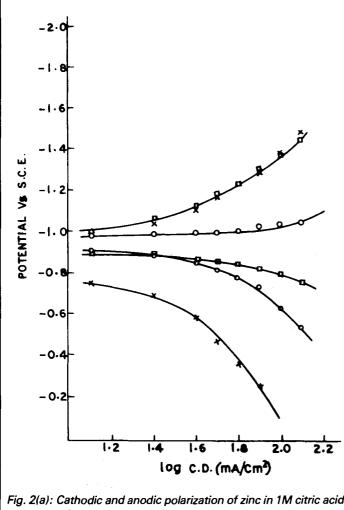
Fig. 2: Cathodic and anodic polarization of zinc in 1M citric acid -- • - • - • - 1M citric acid

The behaviour of narcotine, papaverine, brucine and strychnine on the polarization of zinc in 1M monochloracetic acid is shown in Fig.4, and their effects may be more or less equal on both anodic and cathodic curves. On the other hand, though cinchonidine and quinidine (Fig. 4a) bring about both cathodic and anodic polarization the inhibition brought about by cinchonidine is predominantly under cathodic control.

Quaternary ammonium compounds

Corrosion inhibition

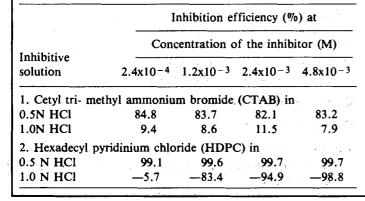
The inhibition efficiency values obtained with CTAB and HDPC in solutions of hydrochloric acid and sulphuric acid are presented in Tables IX and X.

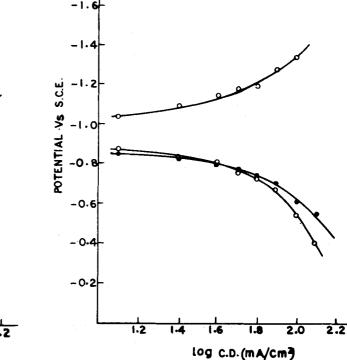


g. 2(a): Cathodic and anodic polarization of zinc in TM citric aci	a
O1M citric acid	
$-\Box$ $-\Box$ 1M citric acid + 4.8 x 10 ⁻³ M brucine	
$- \times - \times - 1M$ citric acid + 4.8 x 10 ⁻³ M strychnine	

Table IX: Inhibition of corrosion of zinc in hydrochloric acid by cetyl trimethyl ammonium bromide and hexadecyl pyridinium chloride

Size of the specimens : 5 cm x 2 cm x 0.15 cmDuration of corrosion test : 2 hours





-1.8

Fig. 3:Cathodic and anodic polarization of zinc in 1M acetic acid $- \circ - \circ -$ 1M acetic acid $- \circ - \circ -$ 1M acetic acid $- \circ - \circ -$ 1M acetic acid + 4.8 x 10⁻³M papaverine

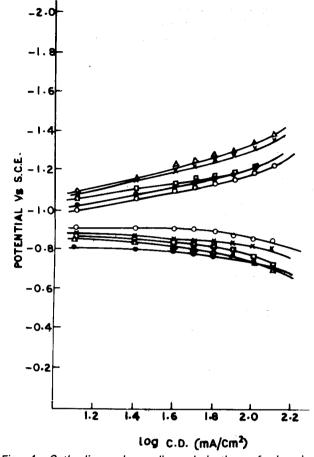
Table X : Inhibition of corrosion of zinc in 1N sulphuric acid by cetyl trimethyl ammonium bromide and hexadecyl pyridinium chloride

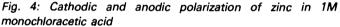
Size of the Specimens : 5 cm x 2 cm x 0.15 cmDuration of corrosion test : 1 hour

	<u> </u>	Inhibition efficiency (%) at Concentration of the alkaloid (M)					
Inhibitive	Con						
compound	2.4x10-4	1.2x10-3	2.4x10 ⁻³	4.8x10-3			
1. Cetyl trimeth ammonium	yl.	1	·. · · ·				
bromide	9.7	48.9	76.3	83.5			
2. Hexa decyl pyridinium		an a					
chloride	97.8	99.3	99.5	99. 7			

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- o o -1M monochloracetic acid
- $-\Delta \Delta 1M$ monochloracetic acid + 4.8 x 10⁻³M narcotine $- \bullet - \bullet - 1M$ monochloracetic acid + 4.8 x 10⁻³M papaverine $- \Box - \Box - 1M$ monochloracetic acid + 4.8 x 10⁻³M brucine $- \times - \times - 1M$ monochloracetic acid + 4.8 x 10⁻³M strychnine

With regard to the corrosion of zinc in 0.5N hydrochloric acid, it is seen from Table IX that with CTAB and hexadecyl pyridinium chloride, the inhibition efficiency values are fairly high and remain almost constant with increase in concentration of the inhibitors. However, hexadecyl pyridinium chloride shows a better performance over CTAB. On raising the concentration of hydrochloric acid to 1N, it is seen that CTAB is not effective (inhibition efficiency - 10%) whereas hexadecyl pyridinium chloride shows incomparably better performance, especially at higher concentrations. With regard to the corrosion of zinc in 1N sulphuric acid it is seen that the performance of CTAB is better than in hydrochloric acid (1N). This may be attributed to the specific role played by the halide ion in the inhibition process. It may be pointed out here that halide ions have been reported to be inhibitive in sulphuric acid [1]. It is interesting to note that hexadecyl pyridinium chloride is found to be equally effective in both the media. Comparing the performance of CTAB (C19 H42 N Br, mol wt. 364.5) and hexa decyl pyridinium chloride (C₂₁ H₃₈ N Cl, mol.

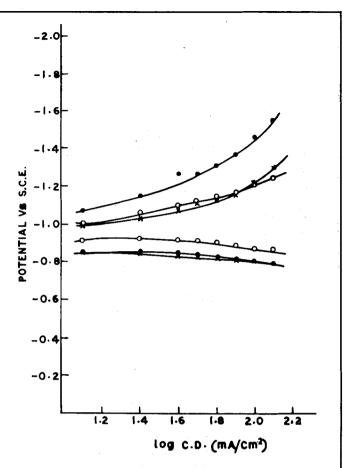


Fig. 4(a): Cathodic and anodic polarization of zinc in 1M monochloracetic acid

 $-\circ -\circ -1M$ monochloracetic acid

 $-\bullet$ $-\bullet$ -1M monochloracetic acid + 4.8 x 10⁻³ M cinchonidine

 $- \times - \times - 1M$ monochloracetic acid + 4.8 x 10⁻³ M quinidine

wt. 357.5) in both the media studied, the enhanced efficiencies of the latter have to be attributed to the presence of a pyridine ring in its molecule as a result of which its adsorption on the metal is more effective through pi-bond interaction [10].

Polarization behaviour

The effects of CTAB and HDPC on the cathodic and anodic polarization behaviour of zinc in 0.5 N hydrochloric acid are shown in Figs.5 and 6.

From Fig. 5, it is seen that both these compounds bring about appreciable cathodic polarization. It is noted from Fig. 6 that CTAB also brings about anodic polarization, as such the action of HDPC is mainly under cathodic control while that of CTAB is under mixed control. Similar conclusions can also be drawn from the results presented in Figs. 7 and 8 with regard to the effect of these compounds on the polarization behaviour of zinc in 1N sulphuric acid.

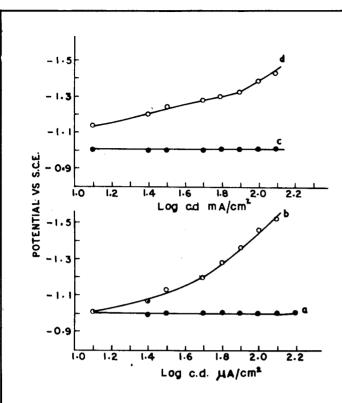
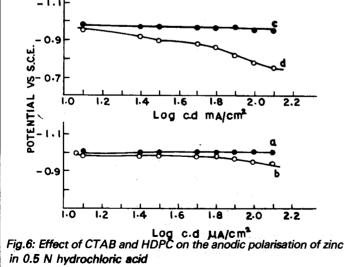


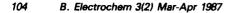
Fig. 5: Effect of CTAB and HDPC on the cathodic polarization of zinc in 0.5 N hydrochloric acid

a, c - 0.5 N Hydrochloric acid b - 0.5 N Hydrochloric acid + 4.8×10^{-3} M HDPC d - 0.5 N Hydrochloric Acid + 4.8×10^{-3} M CTAB

CONCLUSION

Of all the alkaloids examined in this study papaverine shows a relatively high degree of corrosion inhibition whereas the performance of narcotine, an alkaloid of the same group is less effective in all the organic acids. The nux vomica alkaloids, brucine and strychnine are effective in tartaric and citric acids whereas their





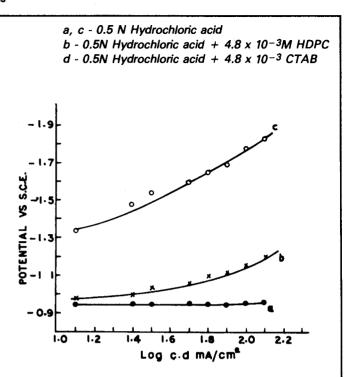


Fig. 7: Effect of CTAB and HDPC on the cathodic polarization of zinc in 1N sulphuric acid

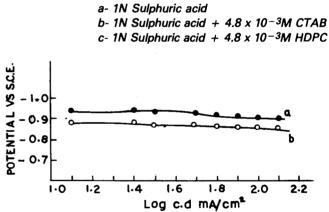


Fig. 8: Effect of CTAB and HDPC on the anodic polarisation of zinc in 1N sulphuric acid

a- 1N Sulphuric acid b- 1N Sulphuric acid + 4.8 x 10^{-3} M HDPC and also for 1N Sulphuric acid + 4.8 x 10^{-3} M CTAB

performance is poor in acetic and propionic acids compared with the inhibition brought about by them in monochlor- and dichloracetic acids. Though to a lesser extent ephedrine is effective only in citric and propionic acids, cinchonidine and quinidine are effective at higher concentrations in mono-and dichloracetic acids. The highest degree of inhibition is shown by papaverine uniformly at all the concentrations in monochloracetic acid. This result is comparable with the performace of hexadecyl pyridinium chloride in hydrochloric and sulphuric acid media. In the case of CTAB

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in 0.5N hydrochloric acid and in sulphuric acid at high concentrations the inhibitive performance is significant. In view of the compounds possessing bactericidal properties in addition, their usage may be preferred for application as inhibitors in corrosive media where biological growths are to be controlled.

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