EFFECT OF CHELATING 8 - HYDROXYQUINOLIN DERIVATIVES ON THE CORROSION OF ZINC IN POLYBASIC ACIDS

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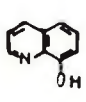
The corrosion behaviour of zinc in some polybasic acids covering a wide range of pK's has been studied. Not only the strength of acid is responsible for the variation in corrosion rate of zinc but also the affinity of acid molecule to form a complex with the corroded zinc ions. The effect of 8-hydroxyquinoline and some of its derivatives on the corrosion of zinc in presents of the polybasic acids (malonic and citric) as aggresive media has been investigated. The weight loss measurements and galvanostatic polarization studies showed that while the hydrazinosulphonyl derivative give a slight inhibition action, all the other derivatives accelerate the corrosion rate.

The effect of large number of organic compounds on the corrosion of zinc in different acid solutions was studied by many authors [1-7]. They observed that the addition of such compounds give an inhibition action which displaced the potential of zinc to more positive values. They attributed the inhibition action to the absorption of organic molecules on the surface of the metal making the inhibitor a part of the Helmholtz double layer.

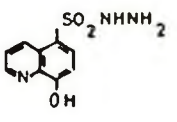
The inhibiting action of possible chelating groups on the corrosion of zinc was investigated by Leroy[8]. He found that although ortho-, meta- and para- amino phenols are capable of chelation with zinc, none of these compounds was sufficiently effective.

8-Carboxy or 8-hydroxy quinoline or its 2-methyl, 2-hydroxy-4-methyl or 8-hydroxy-5-sulfo derivatives were found to inhibit effectively the corrosion of zinc in diluted H_2SO_4 solution [9]. In general these reagents form metal complexes with zinc in solution; these complexes have a weak inhibitive effect.

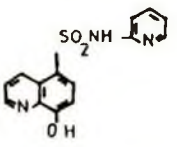
Sulphonamide and sulphonyl derivatives of 8-hydroxy quinoline are of great importance in many medical[10] and biological fields [11,12]. The work given in this article is devoted to examine the effect of the following hydroxyquinolines on the corrosion behaviour of zinc in presence of some polybasic acids.



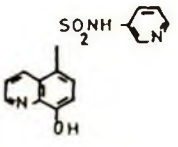
(a) 8-hydroxyquinoline



(b) 5-sulphonyl hydrazide 8-hydroxyquinoline



(c) 5-sulphonyl 2(amino - pyridino)-8-hydroxy-quinoline



(d) 5-sulphonyl-3-(amino pyridino)-8-hydroxy-quinoline

EXPERIMENTAL

The effect of polybasic organic acids as aggresive media in presence and absence of 8-hydroxyquinoline derivatives on the corrosion rate of zinc metal was carried out using weight loss technique [13]. Each experiment was carried out with 50 ml of the aerated corroding solution and without stirring at 30 ± 1°C. All corrosion tests were made in duplicate.

The shift in anodic potentials at zinc metal surface and Tafel constant were determined by anodic galvanostatic polarization studies.

RESULTS AND DISCUSSION

Weight Loss Measurements

The effect of different di- and tri- carboxylic acids on the corrosion rate of zinc metal is recorded in Table 1. It is evident that the rate of corrosion decreases in the presence of acids according to the following order.

Phthalic > malonic = citric > succinic > tartaric

This order is in accordance with decreasing acidity (except for the case of tartaric acid) in

TABLE 1

EFFECT OF DIFFERENT ACID CONCENTRATIONS ON THE CORROSION RATE OF ZINC AT 30 ± 1°C

No.	Concentration M	Rate of corrosion, g/m² /hr.				
		succinic		citric		
		molonic		phthalic		tartaric
1	1.0	16.0	6.0	25	16	3.0
2	0.7	9.5	6.0	20	10.5	2.0
3	0.5	8.0	4.5	18	7.5	0.5
4	0.3	5.3	3.0	21.5	6.0	0.5
5	0.1	3.5	2.0	8.5	4.0	2.5
6	0.05	3.0	1.35	8.0	3.0	2.5

the same direction. As the acidity of the aggresive medium increases, the rate of cathodic hydrogen evolution reaction is increased. These acid anions can also complex with Zn^{++}; the corroded Zn ions will be masked from the corrosion medium by the chelation action of the acids used[14]. This causes a further dissolution of metal, i.e. an increase in the rate of corrosion is observed. The behaviour of tartaric acid can be correlated to its molecular structure. The complexed tartaric acid with two OH groups may have a high adsorption character, and so it may act as a cathodic inhibitor by retarding the hydrogen evolution reaction, and also by covering the metal surface, mainly at the active sites (dis-activating coverage), decreasing any further dissolution of metal.

The corrosion behaviour of zinc metal in the above acids containing 8-hydroxyquinoline and its derivatives has been investigated. The rate of corrosion varies apparently with the change in the molecular structure of the organic additive and also with changes of the concentration (cf. Table 2). At the same concentration, the rate of corrosion in presence of organic additives decrease in following order a > c > d > b.

All these organic molecules have a good chelating tendancy with Zn^{++} ion, but the amount and stability of the chelate to be formed varies with the organic molecule. In all these organic molecules, an intramolecular H-bond exists within the quinolinol moiety and its strength depends on the nature of sulphonyl substitution attached to the molecule. As it would be expected, the stability of the metal chelate increases as the strength of the intramolecular H-bond is decreased, i.e as the ionisation of the phenolic OH being easier. In compounds c, d and b, the sulphonyl substitution, with its electron withdrawing character, decreases the electron density on the phenolic oxygen atom and thus these three derivatives form more stable chelates relative to the unsubstituted 8-hydroxy-

TABLE 2

EFFECT OF THE CONCENTRATION OF ORGANIC ADITIVES (a,c,d,b) ON THE CORROSION RATE OF ZINC METAL IN PRESENCE OF MALONIC AND CITRIC ACIDS (0.5 M) AT 30 ± 1°

Concentration mM	Corrosion rate in (g/m² /hr. Malonic a	c	d	b	Citric acid a	c	d	b
25	41.0	23.0	20.5	8.0	30.0	42.0	21.5	8.0
10	39.0	21.0	16.0	7.0	29.1	26.5	15.0	4.0
5	30.0	20.0	15.0	6.0	21.0	19.5	13.0	3.0
2.5	29.0	10.0	9.0	4.5	17.0	12.5	10.0	2.0
1	29.0	9.0	6.5	4.5	14.0	15.5	8.2	1.5
0	(8.0)	(8.0)	(8.0)	(8.0)	(7.5)	(7.5)	(7.5)	(7.5)

quinoline (compound a). This in turn leads to an increase in the amount of adsorbed chelates on the surface of the zinc metal and concequently decreases the rate of corrosion. Further, the electron withdrawing character of the substitution in compounds c and d is expected to be partially compansated by contribution of the lone pair of electrons of the pyridine nucleus. Such a contribution is more effective in compound (c) with ortho substitution than in compound (d) with substitution in meta position. Therefore, the phenolic OH group in compound (d) is more acidic than that in compound (c), and so the concentration and stability of the metal chelates of compound (d) are higher than those of compound (c).

The decrease in the rate of corrosion in presence of compound (b) is highest. It is probable that the primary amine in the side chain might form salt in the media used. The quaternary nitrogen formed increases the electron withdrawing character of the substitution to a large extent. This in turn facilitates the ionisation of the OH group resulting in increase of both the concentration and the stability of the chelates formed. These are then adsorbed on zinc metal surface causing the observed inhibition.

It is found (Table 2) that the rate of corrosion decreases as the concentration of organic additive is decreased. This behaviour comes in harmony with the above explanation where the concentration of the chelates to be formed will be decreased in the same direction. Also, this behaviour confirms the attribution that metal chelate formation is the main role played by the used organic compounds.

Polarization Studies

The influence of current density on the anodic galvanostatic potential of zinc in 0.5 M malonic and citric acids has been studied in the absence

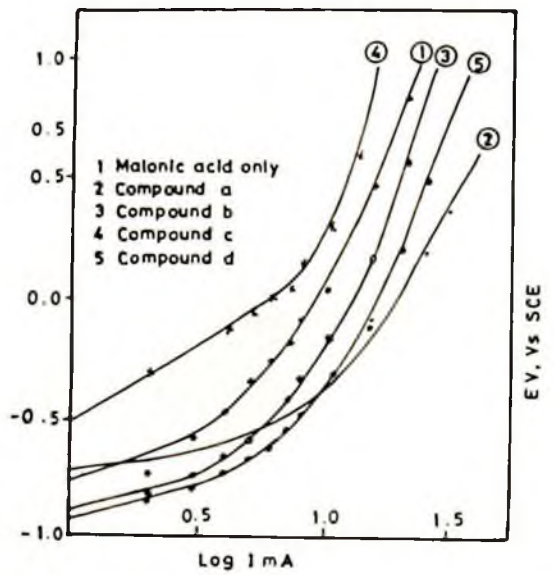


Fig. 1 Effect of organic additives on the anodic galvanostat polarization curves of zinc metal in malonic acid 0.5 M.

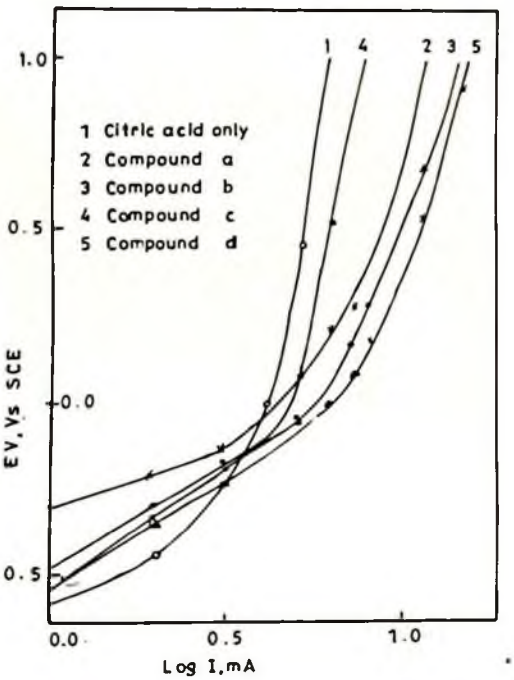


Fig. 2 Effect of organic additives on the anodic galvanostatic polarization curves of zinc metal in 0.5 M citric acid

and presence of organic additives (Figs. 1,2). The Tafel parameter evaluated from polarization data is given in Table 3. From Table 3 it is evident that the value of transfer coefficient is the higher in presence of 8-hydroxyquinoline (compound a) and is the lower one in presence of compound (b).

TABLE 3

THE EFFECT OF ORGANIC ADDITIVES ON TAFEL CONSTANTS FOR ANODIC PROCESS OF ZINC IN 0.5 M MALONIC AND CITRIC ACIDS

Organic additive	Malonic acid			Citric acid		
	a	b^*	α	a	b^+	α
Nil	0.75	0.43	0.07	0.58	0.43	0.07
a	0.7	0.2	0.15	0.3	0.33	0.09
b	0.87	0.35	0.085	0.54	0.64	0.047
c	0.5	0.69	0.04	0.48	0.59	0.05
d	0.89	0.32	0.10	0.54	0.59	0.05

The curves consist of two portions. At low current densities, the potential is slightly shifted to less negative values, with increasing current density. At a certain current density, which varies with additives, the potential shifts more rapidly with current density to much less negative values.

Application of an external current inhibits the process of corrosion. This can only occur in the region of rapid shift in potential with current density. This value of current, where change in potential becomes rapid, is termed the inhibition current.

It is clear from the anodic polarization curves that, the inhibition current is increased by addition of the studied quinolinol and its derivatives than that in absence of them. Therefore, these compounds will accelerate the corrosion process as shown in the part of weight loss measurements.

Generally, the acceleration of corrosion process by 8-hydroxyquinoline and its derivatives (except for the case of compound b) is apparent from the shift of potential to more negative values in presence of these compounds than in their absence, expecially at higher current densities and the values of inhibition current support this.

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