Inhibitive Effect of Pyridine Derivatives on the Corrosion of Zinc in Perchloric Acid

Hesham Mansour, Gaber A. Noubi and Mostafa H. Abu-Elwafa

Chemistry Department, Qena Faculty of Science, Assiut University, Qena, Egypt.

The study of the effect of pyridine, pyridine-3-aldehyde pyridine-4-aldehyde and 4-amino pyridine on the corrosion of zinc in 0 5 M perchloric acid shows that all these compounds retard the dissolution of zinc in $HClO_4$ solutions. The inhibition efficiency can be arranged in the following order:

4-amino pyridine > pyridine > pyridine-4-aldehyde > pyridine-3-aldehyde. All the studied compounds acted as cathodic inhibitors. The influence of parameters like inhibitor concentration, time of immersion and temperature has been also investigated.

Nitrogen containing organic compounds have been found to be very effective as corrosion inhibitors(1-5). An extensive review of the literature has shown that the adsorption of pyridine and its derivatives on mercury have been reported(6,7) but very few studies have been reported on the other metallic surfaces. The inhibitive effect of pyridine,2:6 lutindine and 2:4:6 collidine on the corrosion of iron in HCl has been studied(8) and the reported inhibition efficiency is very small.

Rudresh and Mayanna(9) studied the inhibitive effect of aliphatic amines on the corrosion of zinc in perchloric acid. They found that amines acted as cathodic inhibitors with a small degree of anodic control.

This communication reports the effect of pyridine and some pyridine derivatives on the corrosion of zinc in perchloric acid from weight loss and polarization measurements.

EXPERIMENTAL

The chemicals used were Analar or extrapure quality. All the solutions were prepared in bidistilled water. Zinc (99.998 %) was fixed in Tygon tubing and polished on 4/0 emery paper. The surface was cleaned thoroughly with bidistilled water and acetone in each experiment. The weight loss technique(10) was used for determining the corrosion rate of zinc. The experiments were carried out in an air thermostat and the temperature was adjusted at 25°C ± 0.1. The inhibition efficiency was calculated.

Galvansotatic polarization measurements were made with and without inhibitors. All the potentials were measured with reference to SCE at 25°C ± 0.1.

RESULTS AND DISCUSSION

The calculated corrosion rate of zinc are recorded in Table 1. It is seen that the corrosion rate increases with increasing acid concentration.

TABLE 1

EFFECT OF PERCHLORIC ACID CONCENTRATION ON THE WEIGHT LOSS OF ZINC (mg./sq.dm./hr.) AT 25°C.

Conc.,M	0.1	0.2	0.3	0.4	0.5
Weight loss	92	156	218	297	402

Table 2 shows the effect of pyridine, pyridine-3-aldehyde, pyridine-4-aldehyde and 4-amino pyridine at different concentrations on zinc dissolution in 0.5 M perchloric acid. It is seen that the addition of the studied compounds up to 50 mM retard the corrosion of zinc in perchloric acid. The protection of these additives at a given concentration were in the order:

4-amino pyridine > pyridine > pyridine-4-aldehyde > pyridine-3-aldehyde.

The inhibitive action of these nitrogen containing compounds could be ascribed to its adsorption on zinc surface. The adsorption of pyridine and its derivatives on the metallic surfaces may be expected to be easy because of the aromatic nature and presence of the hetero nitrogen atom which in turn leads to a considerable inhibitive effect. The low inhibition efficiency observed (Table 2 2) for pyridine-3-aldehyde and pyridine-4-aldehyde may be due to the high reducibility of these two compounds.

TABLE 2

EFFECT OF INHIBITOR CONCENTRATION ON THE WEIGHT LOSS OF ZINC (mg./sq.dm./hr.) IN 0.5 M $HClO_4$ AT 25°C(Values in brackets show % inhibition)

Inhibitor Conc., mM	pyridine	pyridine-4-aldehyde	pyridine-3-aldehyde	4-amino pyridine
0.0	402	402	402	402
5.0	320 (20.4)	390 (2.9)	399 (0.74)	288 (28.3)
10.0	282 (29.8)	355 (11.6)	372 (7.4)	257 (42.5)
15.0	260 (35.3)	324 (19.4)	335 (16.6)	231 (42.5)
20.0	234 (41.8)	299 (25.6)	298 (25.8)	202 (49.7)
30.0	198 (50.7)	265 (34.0)	271 (32.5)	171 (57.4)
50.0	153 (61.9)	225 (44.0)	238 (40.7)	139 (65.4)

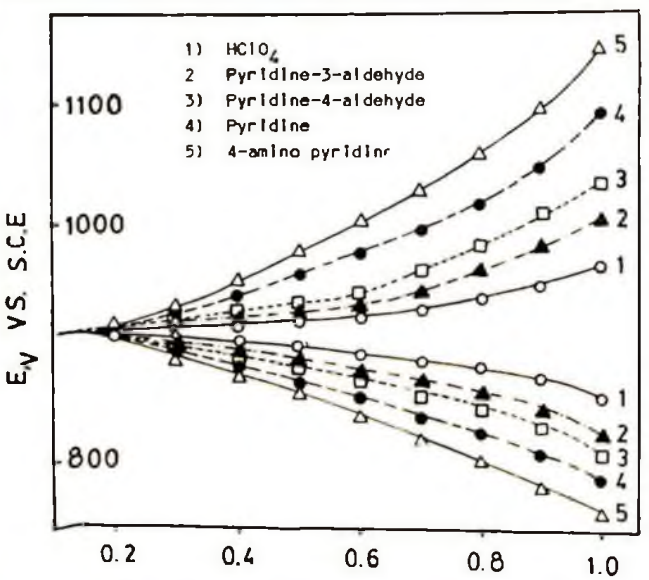


Fig. 1 Influence of current density on cathode and anode potentials of zinc in 0.5 M $HClO_4$ in absence and presence of 50 mM of inhibitors at 25°C .

The high inhibition efficiency of 4-amino pyridine with respect to pyridine could be attributed to the presence of $-NH_2$ donating group. This is supported by a recent study(12) on the inhibitive effect of compounds containing donating groups on zinc dissolution.

POLARIZATION STUDIES

Anodic and cathodic polarization of zinc were carried out in 0.5 M $HClO_4$ in absence and presence of inhibitors(50mM). Fig. 1 shows that both the anodic and cathodic polarization increased by inhibitor concentration and the nature of the inhibitor. The anodic Tafel slope (15± 5mV) in 0.5 M $HClO_4$ is approximately the same in the absence and presence of the inhibitors. Cathodic Tafel slope (20 ± 2mV) in 0.5 M $HClO_4$ increased to 23 ± 2 mV, 25 ± 2 mV, 40 ± 2 mV and 45 ± 2 mV by the addition of 50mM of pyridine-3-aldehyde, pyridine-4-aldehyde, pyridine and 4-amino pyridjne respectively. This may be explained on the basis that these inhibitors play a great part in the cathodic reactions while the anodic reactions are unaffected. This is in good accordance with the fact that nitrogen containing organic compounds decrease the corrosion rate by increasing the hydrogen overvoltage on the corroding metal(13).

The corrosion of zinc (mg./sq.dm.) in 0.5 M $HClO_4$ in the absence and presence of inhibitors was measured as a function of time. Table 3 shows that the corrosion of zinc in 0.5 M $HClO_4$ and inhibition efficiency increases with time in all cases.

TABLE 3

EFFECT OF TIME ON WEIGHT LOSS OF ZINC (mg./sq.dm.) IN 0.5 M $HClO_4$ IN ABSENCE AND PRESENCE OF 50mM OF INHIBITORS. (Values in the brackets show % efficiency)

Inhibitor	Time in hours			
	1/2	1	2	3
Nil	208	402	650	918
Pyridine	115 (44.7)	153 (61.9)	225 (65.3)	298 (67.5)
Pyridine-4-aldehyde	128 (38.4)	225 (44.0)	357 (45.0)	483 (47.3)
Pyridine-3-aldehyde	144 (30.7)	238 (40.7)	275 (42.3)	513 (44.1)
4-amino pyridine	96 (53.8)	139 (65.4)	175 (73.0)	192 (79.0)

This behaviour could be attributed to the consumption of the acid during the corrosion process. Another factor may be the effect of pH change in corroding medium on the rate of complexation between zinc and inhibitors. This

factor is in accordance with the data published by F. Baslo(14). Fig. 2 shows the variation of corrosion potential of zinc in 0.5 M $HClO_4$ in the absence and presence of the studied inhibitors. It is clear that from this figure the potential shifted towards more noble direction with time and attained steady value within 50 minutes.

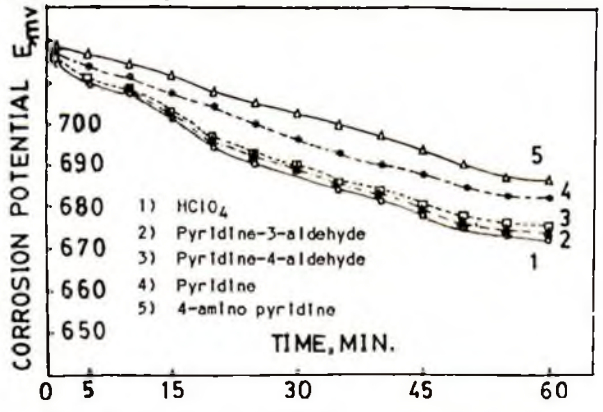


Fig. 2 Influence of time on the Corrosion potential of zinc in 0.5 M $HClO_4$ in absence and presence of 50 mM of inhibitors at 25°C.

The corrosion rates of zinc in 0.5 M $HClO_4$ at different temperatures (Table 4) show that the corrosion rate increases with rising temperature of the corroding medium. The corrosion rate in the range 0-50°C obey the Vant Hoff's and Arrhenius laws.

TABLE 4

EFFECT OF TEMPERATURE ON THE WEIGHT LOSS (mg./sq.dm./hr) OF ZINC IN 0.5 M $HClO_4$.

Temperature	25	30	40	50
Weight loss	402	455	596	662

CONCLUSIONS

It is seen that :

i - Pyridine is a good inhibitor for zinc.

ii - Derivatives of pyridine containing electron withdrawing group(-CHO) possesses low inhibition efficiency than pyridine itself. While derivatives containing electron donating group ($-NH_2$) are more effective to retard zinc dissolution than pyridine.

REFERENCES

1. F.M. Donahane, A. Akiyama and K. Nobe, J. Electrochem. Soc., 114, (1967) 1006.
2. M.N. Desai, Y.B. Desai and M.H. Gandhi, Corrosion Science 9, (1969) 65.
3. S.M. Mayanna, and T.H.V. Setty, Corrosion Science; 15, (1975) 627.
4. M.N. Desai, S.M. Desai and D.K. Shah, Trans. SAEST; 6, (1971) 93.
5. R.L. Leroy, Corrosion; 34, (1978) 98.
6. E. Blomgran, and J.O.M. Bockris, J. Phys. Chem., 63, (1959) 1475.
7. B.E. Conway, and R.G. Barradas, Electrochim. Acta; 5, (1961) 319.
8. R.C. Ayers, and N. Hackerman, J. Electrochem. Soc., 110, (1963) 507.
9. H.B. Rudresh, and S.M. Mayanna, J. Electrochem. Soc., 4, (1982) 109.
10. U.R. Evans, The Corrosion and Oxidation of Metals, p.178, Edward Arnold, London (1960).
11. P. Gupta, R.S. Chaudhary, T.K.G. Namboodhiri, B. Prakash and B.B. Prasad, J Electrochem. Soc., 1, (1983) 27.
12. J. O'M Bockris, and B.E. Conway, J Phys. Chem., 53, (1949) 527.
13. F. Baslo, and R.G. Pearson, Mechanisms of Inorganic Reactions, (2nd Ed.) J. Wiley, London (1967).