EFFECT OF SOME PYRIDINE COMPOUNDS ON THE CORROSION OF ALUMINIUM

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ABSTRACT

The inhibitive effects of pyridine, 2:6 lutidine, 2:4:6: collidine and n-hexadecyl pyridinium chloride on the corrosion of aluminium in hydrochloric acid, phosphoric acid and in sodium hydroxide solution have been studied. All the compounds give better performance in hydrochloric acid than in phosphoric acid and in alkali. It is found that n-hexadecyl pyridinium chloride is more effective than the other compounds in the acids but not in alkali. The performance of the inhibitors being poorer in alkali than in hydrochloric acid may be attributed to the much higher negative potential of aluminium and much larger evolution of gas in alkali which may be unfavourable for the absorption of pyridine compounds.

INTRODUCTION

Pyridine and its derivatives may be expected to get easily adsorbed on metallic surfaces because of their aromatic nature and the presence of the hetero-nitrogen atom, the charge density of which can be varied by substitution of various radicals. Several studies of the adsorption of pyridine and its derivatives on mercury have been reported, [1-6] but very few on solid metal surfaces. Even so, the systems studied [7,8] happen to be those in which there are no complications like gas-evolution or a high corrosion rate. From the practical point of view, it would be more appropriate to study the effect of inhibitive substances in corroding than in quiscent media. From this point of view, the study of methyl pyridines with respect to the corrosion of iron in hydrochloric acid is re-reported [9] to indicate that the adsorption of neutral species accounts for the differences observed in inhibition depending upon the number of methyl substituent groups, though it cannot be said whether the cation or the free amine is responsible for the inhibition.

In the light of this report, it appeared worthwhile to study the effect of pyridine, of two of its methyl derivatives, namely, 2:6 lutidine and 2:4:6 collidine and of n-hexadecyl pyridinium chloride on the corrosion of aluminium in hydrochloric acid, phosphoric acid and in alkali, since in these media, aluminium was appreciably attacked unlike in nitric acid and sulphuric acid. The observations of the study are reported in this paper.

EXPERIMENTAL

1. Materials

(i) *Metal specimens:* Specimens of size 3″ × 1″ × 1/16″ of alumium (not less than 99% purity) were used for determination of corrosion rate.

(ii) Circular specimens of 1 cm. dia. with 10 cm. long stem were used for polarization studies. The specimens were polished with Ronuk's emery compound and degreased with trichloroethylene.

2. Chemicals:

Hydrochloric, sulphuric, phosphoric and nitric acids and caustic soda, all of A.R. grade, were employed for making up the required solution in distilled water. The organic compounds were of L. R. Grade.

PROCEDURE

Corrosion rate:

The corrosion rate of aluminium in the different media was determined by weight loss measurements In each experiment, specimens were immersed in 750 ml. of the solution for 2 hours and the average of the four weight loss measurements was taken.

Polarization

The cathodic and anodic polarization of aluminium was studied in 1.1 N hydrochloric acid solution in which measurable corrosion inhibition was observed. For carrying out the experiment, the circular specimen stopped off with Americo lacquer so as to expose only one side of the circular portion, was immersed in 400 ml. of the solution. After measuring the initial potential, the polarization was carried out by impressing known values of current drawn from a constant direct current source through a series of high resistances. A platinized platinum sheet of 6.25 sq. cm. area was employed as the auxiliary electrode. The potentials were measured by means of a vacuum-tube voltmeter (D.C. Micro-voltmeter-Philips Model G. M. 6020). The experiments were carried out at room temperature of 26°C.

RESULTS AND DISCUSSION

The inhibition of corrosion of aluminium in 1.1 M. hydrochloric acid by various methyl substituted pyridine compounds is shown in Table 1. It is seen that contrary to expectation, the inhibition given by lutidine (II) or collidine (III) is no higher than that given by pyridine except in the case of 1.0% lutidine. On the other hand, n-hexadecyl pyridinium chloride (IV) gives better inhibition at all the three concentrations. This may be attributed to the adsorption by coulombic interaction between the positively charged pyridinium ion and the metal surface. It may also be seen from Fig. 1, that there is pronounced cathodic polarization of aluminium in HCl in the presence of IV, compared to that in the presence of the other compounds. Incidentally, it may be noted that in the case of I, there is actually a slight depolarization after initial cathodic polarization. It is possible that under the conditions of the experiment, pyridine is susceptible to cathodic reduction. That all these compounds act cathodically is also substantiated by the fact that there is negligible anodic polarization of aluminium in their presence in HCl as indicated in Fig. 2. It has been pointed out by Ayers and Hackerman[9] that inhibition increases with the number of methyl groups substituted in the pyridine ring and that if free amine were not involved, one would not expect this correlation between inhibition and substitution effects. Since such a correlation is not observed in the case of inhibition of corrosion of aluminium in HCl, it would appear that molecular adsorption is not the main reason for the various inhibitive effects of the compounds studied. However, if the inhibition of corrosion of iron by I, II and III in HCl as reported by Ayers and Hackerman is compared with that of aluminium (see Table 3), it is observed that for inhibitor-concentrations of the same order, the values of inhibition efficiency are higher for aluminium than for iron. This variation in the performance of the inhibitors can be attributed to the differences in the charge of the metals in the respective solutions. It has been pointed[9] out that the corrosion potential of iron is believed to be 0.25 V negative to its zero charge potential. On the other hand, in the case of aluminium 1.1 M hydrochloric acid, the observed corrosion potential of -0.77v versus saturated colomel is very close to the reported zero charge potential of -0.52v versus N.H.E. for aluminium in 0.01 M KCl[10]. Hence, it is reasonable to conclude that the compounds are easily adsorbed on aluminium in HCl displacing the water-dipoles but their adsorption is not favoured on iron having appreciable negative charge. In the case of hexadecyl pyridinium chloride, the uniformly high inhibition efficiency may be due to the fact that the pyridinium ion is attracted and adsorbed on the aluminium surface, which may still have a negative charge, though close to the point of zero charge. The other possibility is that the chloride ion, which is known to be easily specifically adsorbed on metal surfaces acts as a bridge and keeps the pyridinium ion tied to the metal surface.

To elucidate whether the chloride ion may be acting as a bridge, experiments were carried out using the pyridine compounds with aluminium in concentrated phosphoric acid. From Table 2, it is seen that the inhibition in this acid is much lower than that in HCl for the corresponding concentration of the inhibitive substances. This would seem to lend support to the thesis that chloride ion is in some way helpful.

To test this probability further, experiments were carried out with phosphoric acid containing 1% pyridine to which either sodium chloride or hydrochloric acid was added, but in both cases the corrosion of aluminium was not inhibited. It therefore, appears that excess chloride ions available in hydrochloric acid is favourable for inhibition.

The observations made with regard to the inhibition of aluminium in alkaline solution may now be considered. It is seen from Tables, 4, 5 and 6 that no definite trend in the

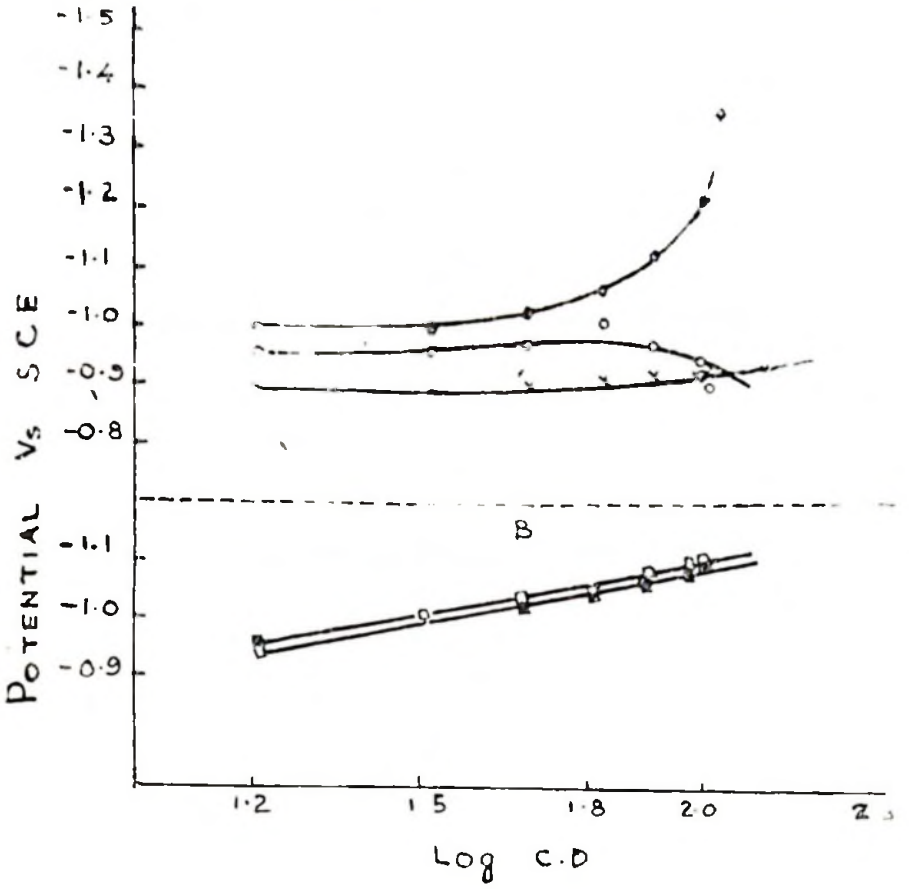


Fig. 1: Cathodic Polarization of Aluminium (25) in Hydrochloric Acid

A * — * 1.1M HCl
○—○ 1.1M HCl + 1% Pyridine
⁘—⁘ 1.1M HCl + 0.1% n-Hexadecyl Pyridinium Chloride

B □—□ 1.1M HCl + 1% 2:6 Lutidine
▣—▣ 1.1M HCl + 1% 2:4:6 Collidine

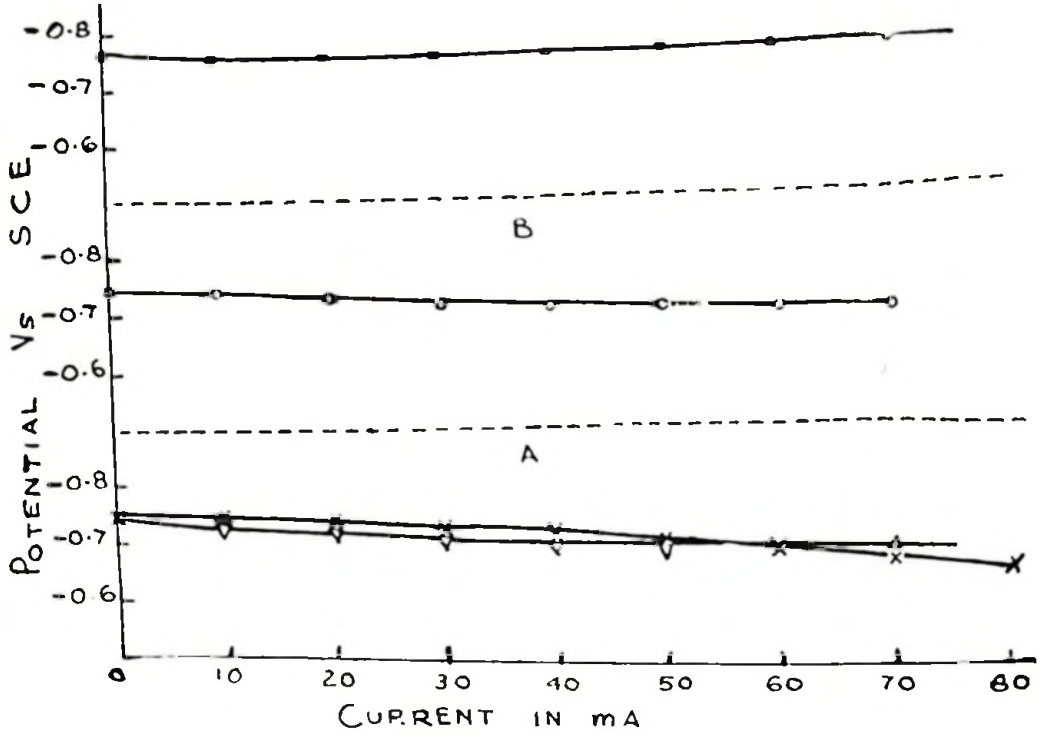


Fig. 2: Anodic Polarization of Aluminium in Hydrochloric Acid

A * — * 1.1M HCl
▽—▽ 1.1M HCl + 1% Pyridine
B ○—○ 1.1M HCl + 0.1% n-Hexadecyl Pyridinium Chloride
1.1M HCl + 1% 2:6 Lutidine also follows the same curve
C ⁘—⁘ 1.1M HCl + 1% 2:4:6 Collidine

TABLE 1

Effect of Pyridine and its compounds on the corrosion of Aluminium in Hydrochloric acid (1.1M) at room temperature

Addition agent	*Inhibition efficiency at concentrations of*		
	0.01%	0.1%*p*	1.0%
1. Pyridine ..	58	40.4	54.5
2. 2:6 Lutidine ..	15.4	11.0	62.5
3. 2:4:6 collidine ..	45.1	41.9	37.5
4. n-Hexadecyl Pyridinium Chloride ..	69.1	86.8	86.4

TABLE 2

Inhibition efficiency of the Pyridine compounds on the corrosion of Aluminium in pure Phosphoric acid (53.2N)

Addition agent at 10% concentration	*Inhibition efficiency (%)*
1. Pyridine ..	10.0
2. 2:6 Lutidine ..	0
3. 2:4:6 collidine ..	–4.0
4. n-Hexadecyl Pyridinium chloride ..	23.3

TABLE 3

Comparison of inhibition of Mild Steel and Aluminium in Hydrochloric acids by methyl derivatives of Pyridine

Inhibitor	*Inhibition of Mild steel in 6.08N HCl with 0.01M inhibitor*	*Inhibition of Aluminium in 1.1M HCl with with 0.1% inhibitor*
1. Pyridine ..	5% inhibitor = 0.08%	40%
2. 2:6 Lutidine ..	10% inhibitor = 0.11%	11%
3. 2:4:6 collidine ..	12% inhibitor = 0.11%	42%

TABLE 4

Effect of Pyridine and its compounds on corrosion of Aluminium in 0.1M NaOH at room temperature

a Time of immersion: 2 hrs. *b* Specimen size: 1" × 3"

Name of the addition agent	*Inhibition efficiency at concentrations of* 0.001%	0.01%	0.1%
1. Pyridine ..	21.2	21.2	19.2
2. 2:6 Lutidine ..	34.6	19.2	25.0
3. 2:4:6: collidine ..	4	0	0
4. n-Hexadecyl-Pyridinium Chloride ..	5.8	17.3	32.7

TABLE 5

Effect of Pyridine and its compounds on corrosion of aluminium in 0.2M. Sodium hydroxide at room temperature

a Time of immersion: 2 hrs. *b* Specimen size: Aluminium 1″ × 3″

Addition agent	*Inhibition efficiency at concentrations of*		
	0.001%	0.01%	0.1%
1. Pyridine ..	15.7	29.4	31.6
2. 2:6 Lutidine ..	11.1	14.1	22.7
3. n-Hexadecyl-Pyridinium chloride ..	21.3	25.6	29.1

TABLE 6

Effect of Pyridine and its compounds on the corrosion of Aluminium in 1M. sodium hydroxide

a Time of immersion: 2 hrs. *b* Specimen size: 1″ × 3″

Name of the addition agent	*Inhibition efficiency at concentrations of*		
	0.001%	0.01%	0.1%
1. Pyridine ..	−1.4	−22.7	−9.1
2. 2:6 Lutidine ..	7.7	−2.8	−12.5
3. n-Hexadecyl Pyridinium Chloride ..	0	0.3	34.0

TABLE 7

Influence of sodium chloride on the corrosion of Aluminium in 0.2M sodium hydroxide containing Pyridine derivatives

Addition agent at 0.1% concentration	*Inhibition efficiency at sodium chloride concentrations of*			
	0	0.03%	0.06%	0.13%
1. 0.2M NaOH alone (no addition agent) ..		−5.0	3.3	−8.3
2. Pyridine ..	31.6	5.0	13.3	−11.7
3. 2:6 Lutidine ..	22.7	11.0	-5.0	5.0
4. n-Hexadecyl Pyridinium Chloride..	29.1	6.6	18.3	11.6

change of inhibition efficiencies with increase in the concentration of alkali is indicated, except that at the highest concentration of 1 M. sodium hydroxide, the efficiencies are radically affected, attaining in some cases even negative values. Considering only Table 4 it is seen that hexadecyl pyridinium chloride is not holding the pride of place as in HCl and that 2:6 lutidine appears to be better than pyridine and much better than 2:4:6 collidine. Again the relative behaviour of the substances cannot be explained in terms of the methyl group substitution. It may be noted that the values of inhibition efficiency in sodium hydroxide solution at the various concentrations do not compare favourably with those obtained in HCl. This would again support the postulate regarding the beneficial role of chloride ions. However, when sodium chloride of various concentrations was added to the sodium hydroxide solution, the effectiveness of any of the inhibitors was not improved as can be seen from Table 7. On the other hand, it was considerably brought down. It would appear from this that the chloride ion is not appreciably adsorbed at the aluminium in alkaline solution either because of the high negative potential or because of the vigorous evolution of hydrogen gas. The relatively poorer performance of hexadecyl pyridinium chloride even when aluminium is appreciably negatively charged as in the alkaline medium points to the brisk evolution of gas on the metal surface as the primary reason. It has been reported [11] that on mercury, surface coverage by 2-methyl pyridine, 2-6 lutidine and 2-4 lutidine did not exceed 0.05 at potentials of cathodic H-evolution.

The relatively lower efficiencies of the other compounds also in alkali as compared to HCl are, perhaps, the result of the highly negative potential of aluminium (–1.44 versus saturated calomel electrode) and the brisk evolution of gas in the alkaline medium).

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