

INHIBITION OF THE ACID CORROSION OF ALUMINIUM BY SOME DERIVATIVES OF THIOSEMICARBAZONE

P.C. Okafor, E.E. Ebenso and U.J. Ekpe*

Department of Pure and Applied Chemistry, University of Calabar, P.M.B 1115, Calabar, Nigeria

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ABSTRACT. The inhibition of corrosion of aluminium in HCl solution by some derivatives of thiosemicarbazones has been studied using weight loss and hydrogen evolution techniques. The thiosemicarbazone derivatives used are 2-acetyl pyridine-(4-phenylthiosemicarbazone) (PTSC), 2-acetyl pyridine-(4-phenyl-iso-methylthiosemicarbazone) (PIMTSC) and 2-acetyl pyridine-(4-phenyl-iso-ethylthiosemicarbazone) (PIETSC). The inhibition efficiency depended on the compounds concentration until at very low concentration studied where they reversed their functions and became accelerators. Kinetic treatment of the results gave a first order type of mechanism. The results reported in this paper elucidate the effects of inhibitor concentration, temperature and the molecular structure on the inhibition efficiency.

KEY WORDS: Corrosion inhibition, Aluminium, 2-Acetyl pyridine-(4-phenylthiosemicarbazone) (PTSC), 2-Acetyl pyridine-(4-phenyl-iso-methylthiosemicarbazone) (PIMTSC), 2-Acetyl pyridine-(4-phenyl-iso-ethylthiosemicarbazone) (PIETSC), Kinetics

INTRODUCTION

Aluminium, though possessing an excellent corrosion resistance has been reported to corrode severely in some solutions [1]. Aluminium and its alloys possess extensive application in mechanical and chemical environments as components in pumps, valves, textile and marine industries. Its corrosion in solution containing chloride ions appears to be of special interest due to the role of chloride ion in destroying the passivity of aluminium surface [2]. It has been established that the use of chemical inhibitors for the corrosion of aluminium and its alloys remains the most practical and cost effective means of preventing corrosion [3].

Thiosemicarbazones (TSC) and its derivatives contain nitrogen and sulphur in its structure and thus have a lot of prospect as corrosion inhibitors. Several studies have been carried out using some derivatives of thiosemicarbazone to inhibit the corrosion of aluminium in hydrochloric acid and sodium hydroxide solutions [4-9]. Some authors have also used thiosemicarbazone and its derivatives as corrosion inhibitors of some metals and alloys [10-22].

In view of the growing interest in recent years in an attempt to abate the acid dissolution of metals, the present investigation is aimed at studying the corrosion of aluminium in HCl solution in the absence and presence of 2-acetyl pyridine-(4-phenyl thiosemicarbazone) (PTSC), 2-acetyl pyridine-(4-phenyl-iso-methyl thiosemicarbazone) (PIMSTC) and 2-acetyl pyridine-(4-phenyl-iso-ethyl thiosemicarbazone) (PIETSC) using weight loss and hydrogen evolution techniques. This study is still a continuation of our extensive studies on the efficiency of thiosemicarbazones and its derivatives as potential corrosion inhibitors.

*Corresponding author. E-mail: ujekpe@yahoo.com

EXPERIMENTAL

Sheets of aluminium used for this study were obtained from System Metal Industries limited, Calabar, Nigeria. The chemical composition of the aluminium sheet used was as follows: Si: 0.15%, Fe: 0.19%, Mn: 0.005%, Mg: 0.1%, Cu: 0.02%, Al: 99.535% and the dimensions of the test pieces were 4 x 5 x 0.045 cm. The specimens were cleaned by scrubbing with bristle brush under the flow of water and degreased in absolute ethanol. They were then dried in acetone and stored in a dessicator [23].

Weight loss technique

Previously weighed aluminium specimen was suspended by a glass look and completely immersed in a 250 mL beaker containing the corrodent at HCl concentrations varying from 0.005 to 0.5 M. The studies were carried out at 30, 40, 50, and 60 °C. The specimens were retrieved from their corrodent at 24 h intervals progressively for 168 h (7 days), immersed in concentrated HNO₃, washed with bristle brush under the flow of water, dried in acetone and reweighed [23].

Further measurements using weight loss technique involved the preparation of five different concentrations (5×10^{-5} to 5×10^{-4} M) of the thiosemicarbazone (TSC) derivatives in 0.1 M HCl solution and used as corrodent for the aluminium specimens. As before, each specimen was retrieved from the solution at 24 h interval, washed and weighed. Duplicated experiments were performed in each case and the mean value of the results recorded. All weights were recorded on Mettler AT 460 (Delta Range) analytical balance to the nearest 0.0001 g.

The inhibition efficiency (% I) of the inhibitors was calculated using the formula.

$$\% I = \left(1 - \frac{W_1}{W_2} \right) \times 100 \quad (1)$$

where W_1 and W_2 are the weight losses for aluminium in the presence and absence, respectively, of the inhibitor in HCl solutions at the same temperature [24].

Hydrogen evolution technique

The gasometric assembly used for the measurement of the hydrogen gas evolution was designed following the method employed by Onuchukwu and Mshelia [25] and also reported by Ebenso *et al.* [22].

RESULTS AND DISCUSSIONS

Effect of corrodent concentration on corrosion of aluminium in HCl solution

Figure 1(a)-(d) shows the variation of weight loss with time for aluminium corrosion in different concentration of HCl solution at 30 - 60 °C. It was observed that weight loss of aluminium increases with increase in acid concentration at a given temperature. The weight loss for 0.5 M HCl solution was far much greater than those obtained for HCl solution with concentration less than 0.5 M. Similar observation was reported by Ibok *et al.* [9] and Patel *et al.* [26]. This could be attributed to increased concentration of the chloride ions in the more concentrated solution, which readily react with the aluminium ions present in the solutions. The formation of aluminium chloride with chloride ion is also corrosive to aluminium.

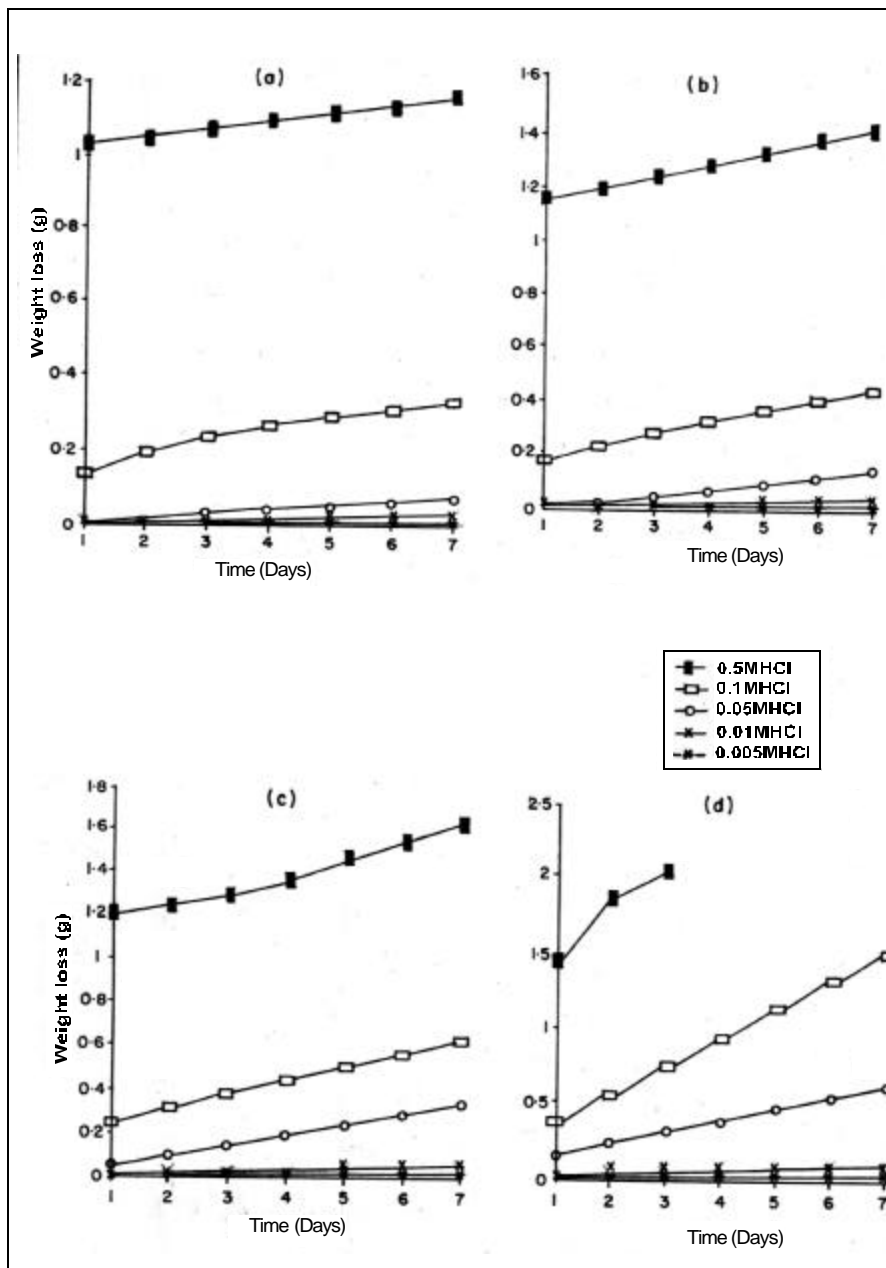


Figure 1. Variation of weight loss with time for aluminium in different concentrations of HCl solution without inhibitor at (a) 30 °C, (b) 40 °C, (c) 50 °C, (d) 60 °C.

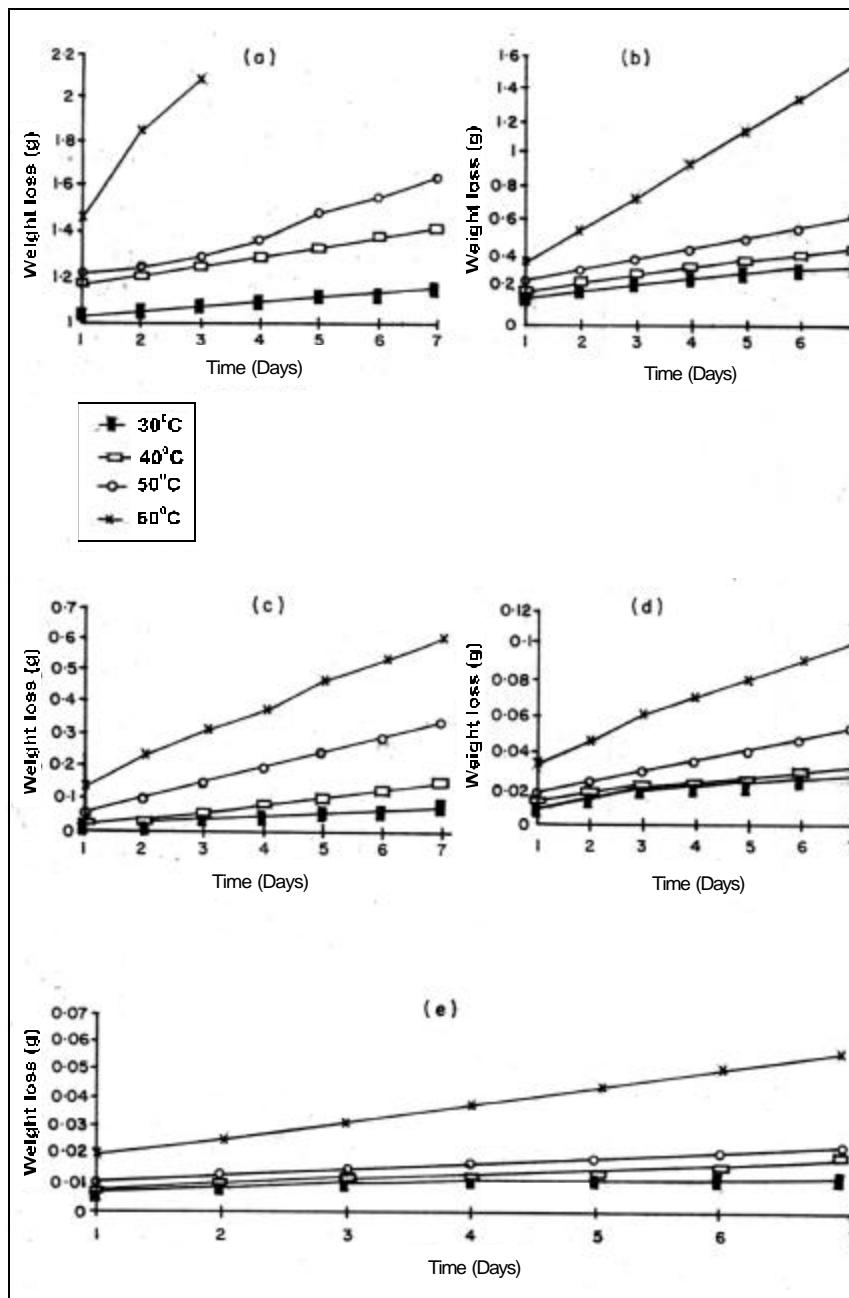


Figure 2. Effect of temperature variation on the weight loss with time for aluminium in HCl (a) 0.5 M, (b) 0.1 M, (c) 0.05 M, (d) 0.01 M, and (e) 0.005 M at different temperatures .

Effect of temperature on corrosion of aluminium in HCl solution

Figure 2(a)-(e) shows the effect of temperature variation on the weight loss with time for aluminium at constant HCl concentrations without inhibitors. For all the plots, there is a progressive increase in weight loss as the temperature increased. This is probably due to increase in the rate of diffusion and ionization, which favours corrosion as the temperature increases [27]. An increase in temperature may also increase the solubility of the protective films and of any corrosion product precipitated [9, 28], thus increasing the susceptibility of the metal to corrosion.

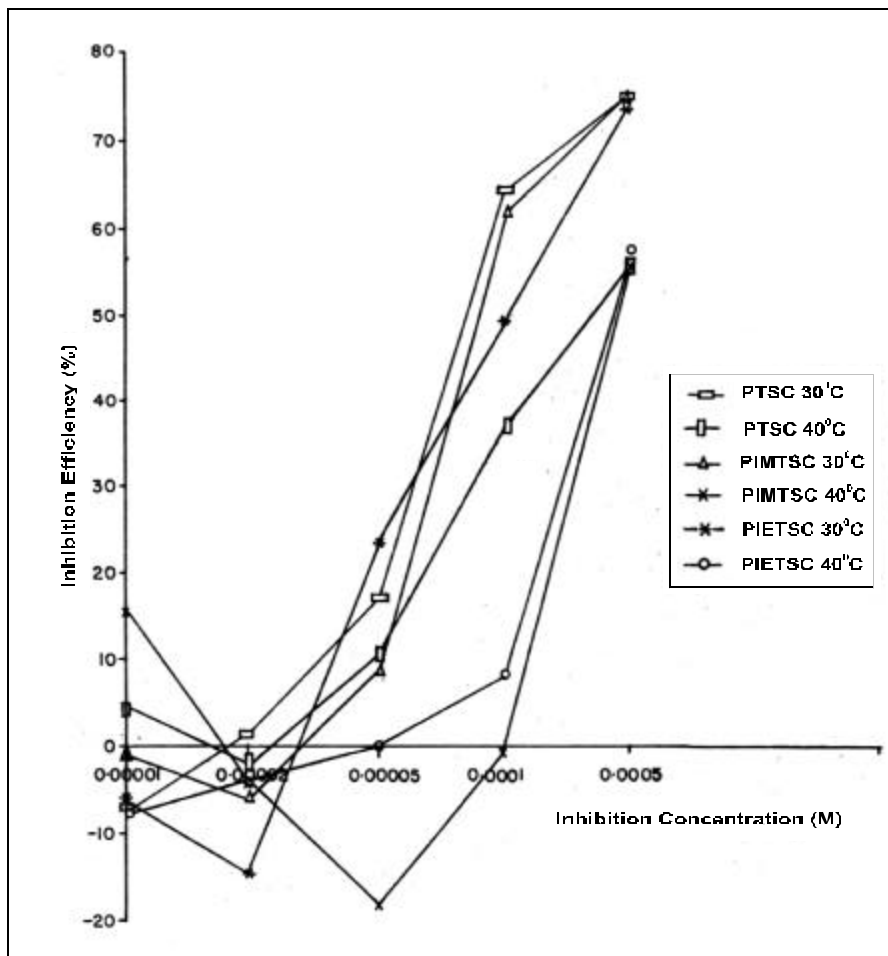


Figure 3. Variation of inhibition efficiency with inhibitor concentration for aluminium in 0.1 M HCl solution containing the compounds.

Inhibitory action of PTSC, PIMTSC and PIETSC

Figure 3 shows that the PTSC inhibits the corrosion of aluminium to an appreciable extent, with inhibition increasing with decreasing temperature and increasing inhibitor concentration. The compounds were generally observed to inhibit better at higher concentrations at all temperatures. At low concentrations; 1×10^{-5} - 2×10^{-5} M for PTSC, 2×10^{-5} - 5×10^{-5} M for PIMTSC and 1×10^{-5} M - 2×10^{-5} M for PIETSC, the compounds rather accelerated the corrosion process. This is probably due to the formation of very weak films of the compounds (or adsorbates) on the aluminium surface which can be easily washed off by the corrosion medium. Similar view was held by other research groups and several studies we have carried out [7, 9, 22, 29-32].

The inhibition efficiencies of the compounds were observed to be affected by temperature. The maximum inhibition efficiencies exhibited by the compounds were observed at 5×10^{-4} M at all temperatures, and is in the order PTSC (75.92%) > PIMTSC (75.89%) > PIETSC (73.58%) at 30 °C. It is worthy to mention here that at concentration of 5×10^{-3} M (higher than the highest concentration reported in this paper) we observed a rather very low inhibition efficiency which indicates that 5×10^{-4} M was the critical concentration.

Hackerman and Makrides [33] proposed that a corrosion inhibitor may function by reaction with the metal ion newly produced in the corrosion environment but in a plane very near or on the metal surface, and by adsorption onto the metal surface. This theory is also being upheld by several other research groups [34-37] who have added slight modifications. The inhibition action of PTSC, PIMTSC and PIETSC are suggestive of adsorption onto the metals surface. There are basically two types of adsorption: physical (physisorption) and chemical (chemisorption). Physical adsorption is by weak interactions only; no covalent bonds occur between the adsorbent and adsorbate; heat of physisorption is usually less than about 80 kJmol⁻¹ [38]. Chemisorption is adsorption involving stronger interaction between adsorbate and adsorbent usually accompanied by arrangement of atoms within or between adsorbates; reaction occur between the surface of the adsorbates and the adsorbent; heat of chemisorption is usually in excess of 80 kJmol⁻¹ [39]. Increase in temperature from 30 to 40 °C was observed to decrease the inhibition efficiencies of the compounds except at very low concentrations where increase was observed. The decrease in inhibition efficiency suggests physical adsorption of the compounds on the aluminium surface. The relatively low average activation energy values of the compounds reported as 41.21 kJmol⁻¹ for PTSC (Table 1), 48.77 kJmol⁻¹ for PIMTSC (Table 2) and 42.88 kJmol⁻¹ for PIETSC (Table 3) for the temperature range of 30 - 40 °C confirms the assertion that the compounds are physically adsorbed on the metal surface.

Table 1. Kinetic data for aluminium in 0.1 M HCl solution containing PTSC from weight loss measurements.

Inhibitor concentration $\times 10^{-4}$ M	Inhibitor efficiency (%)		Rate constant, k (day ⁻¹)		Half-life, $t_{1/2}$ (day ⁻¹)		Activation energy, E_a (kJmol ⁻¹)
	30 °C	40 °C	30 °C	40 °C	30 °C	40 °C	
5.0	75.92 (72.07)	56.12	0.0010	0.0025	675.00	277.20	69.59
1.0	64.36 (-28.82)	37.27	0.004	0.0032	495.00	231.30	67.84
0.5	17.37 (-43.24)	10.84	0.0020	0.0032	346.50	210.00	26.08
0.2	1.55 (-310.85)	-2.20	0.0023	0.0036	310.30	192.50	26.03
0.1	-7.67 (-288.18)	4.48	0.0024	0.0036	288.76	192.50	13.51

Average activation energy = 41.21 kJmol⁻¹. () = Inhibition efficiency (%) values obtained from gasometric method.

Table 2. Kinetic data for aluminium in 0.1 M HCl solution containing PIMTSC from weight loss measurements.

Inhibitor concentration $\times 10^{-4}$ M	Inhibitor efficiency (%)		Rate constant, k (day^{-1})		Half-life, $t_{1/2}$ (day^{-1})		Activation energy, E_a (kJmol^{-1})
	30 °C	40 °C	30 °C	40 °C	30 °C	40 °C	
5.0	75.89 (73.87)	55.64	0.0011	0.0031	630.00	265.00	69.59
1.0	61.9.0 (63.97)	-0.81	0.0015	0.0040	462.00	231.00	67.84
0.5	8.83 (63.30)	-17.85	0.0024	0.0042	288.50	210.00	26.08
0.2	-6.28 (41.44)	-4.26	0.0025	0.0040	277.20	192.50	26.03
0.1	-1.22 (-34.14)	15.53	0.0025	0.0036	277.20	192.50	13.51

Average activation energy = 48.77 kJ mol⁻¹.

Table 3. Kinetic data for aluminium in 0.1 M HCl solution containing PIETSC from weight loss measurements.

Inhibitor concentration $\times 10^{-4}$ M	Inhibitor efficiency (%)		Rate constant, k (day^{-1})		Half-life, $t_{1/2}$ (day^{-1})		Activation energy, E_a (kJmol^{-1})
	30 °C	40 °C	30 °C	40 °C	30 °C	40 °C	
5.0	73.58 (74.77)	57.63	0.0011	0.0025	630.00	277.20	70.24
1.0	49.56 (27.03)	8.14	0.0018	0.0038	485.00	187.30	60.22
0.5	23.66 (-22.52)	0.01	0.0023	0.0040	315.00	182.37	44.74
0.2	-14.73 (-20.52)	-4.06	0.0025	0.0043	301.50	173.25	23.86
0.1	-6.67 (-67.56)	-7.91	0.0022	0.0037	277.20	173.25	15.34

Average activation energy = 42.88 kJ mol⁻¹.

Effect of molecular structure

The differences in inhibition efficiency at a given temperature are attributed to the molecular structure of the inhibitors used. The structure of the compounds proposed [40] are presented in Figures 4. These compounds are similar on two sides of the thiocarbonyl group and different on the third side. PTSC in solution contains hydrogen on the sulphur atom, which was substituted with methyl and ethyl group in PIMTSC and PIETSC, respectively. The molecular mass difference is in the order PIETSC > PIMTSC > PTSC which is the reverse of order of inhibition efficiency. However, observation is contrary to reports that physisorbed inhibitors of high molecular weight inhibit better than lower molecular weight inhibitors.

The difference in activity between the compounds is probably due to the loss in linearity of the structure caused by the presence of the iso-group. The presence of the group distorts the arrangement of the protective coverage on the surface of the metals; and this distortion increases with increase in the size of the iso-group, thus decreasing the inhibition efficiency as molecular weight increases. This explanation indicates that the inhibiting action of the compounds is mainly imparted by the thiocarbonyl group. The absence of iso-group on the thiocarbonyl group favours the Vander Waals forces of attraction between the thiocarbonyl group and the aluminium surface, and increase in size of the iso-group weakens the forces of attraction thereby decreasing the efficiency.

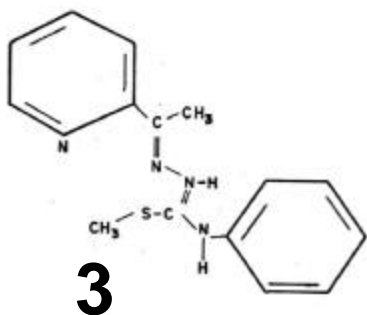
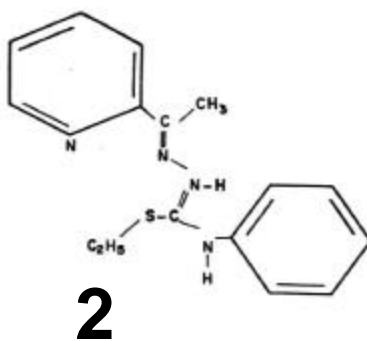
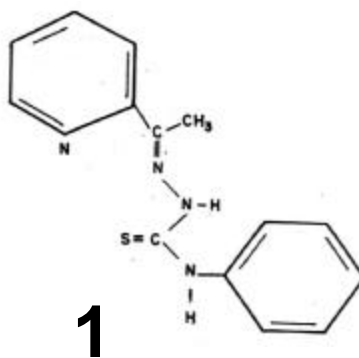


Figure 4. Structure of 2-acetylpyridine-(4-phenylthiosemicarbazone) (PTSC) (1), 2-acetylpyridine-(4-phenyl-iso-methylthiosemicarbazone) (PIMTSC) (2), and 2-acetylpyridine-(4-phenyl-iso-ethylthiosemicarbazone) (PIETSC) (3).

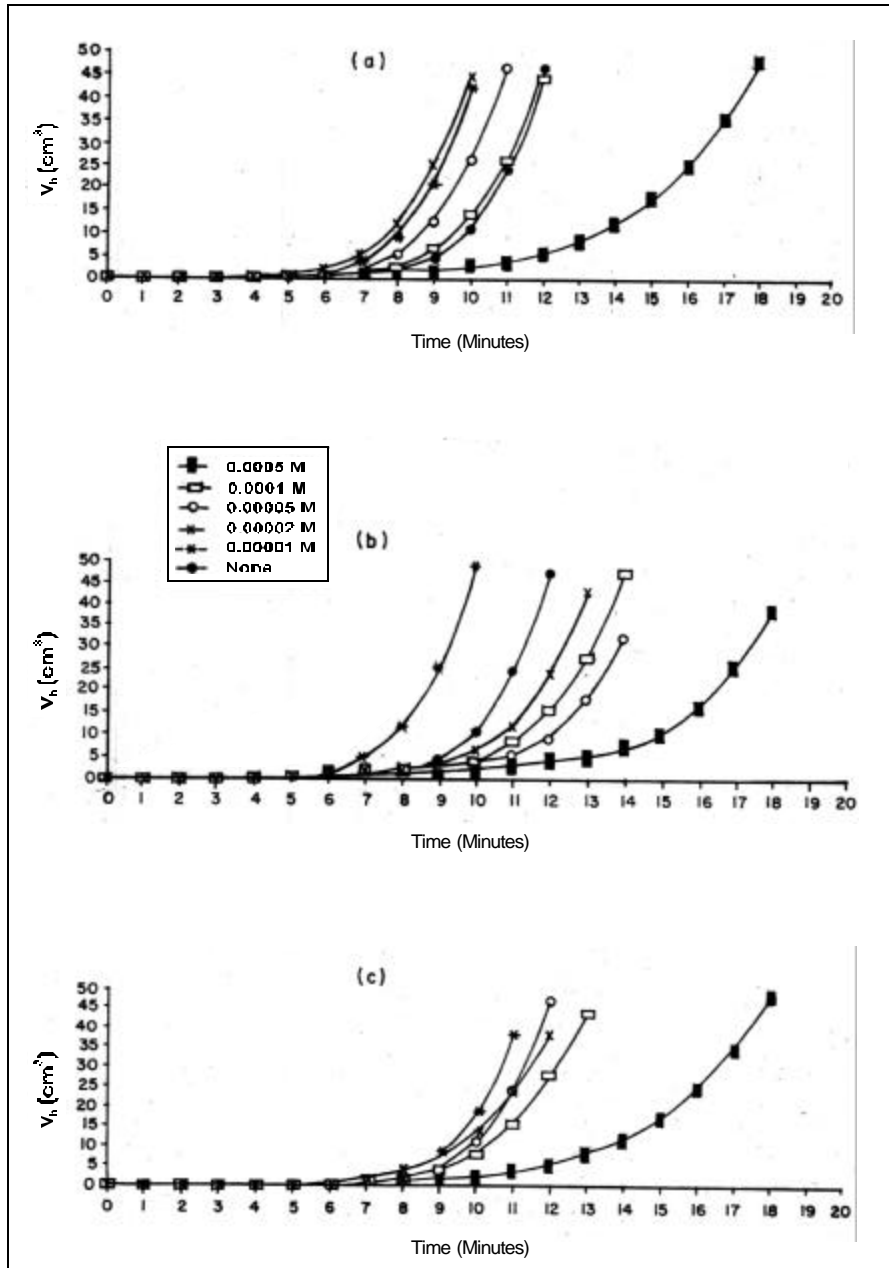


Figure 5. Variation of volume of hydrogen evolved, V_h with time for aluminium in 2 M HCl solution containing (a) PTSC, (b) PIMTSC and (c) PIETSC.

Inhibitory action of PTSC, PIMTSC and PIETSC on corrosion of aluminium in 2 M HCl solution (obtained from gasometric method)

Figure 5(a)-(c) shows the variation of volume of hydrogen evolved with time of exposure of aluminium in 2 M HCl solution containing PTSC, PIMTSC and PIETSC, respectively. It was observed that volume of hydrogen evolved increases with time of exposure of aluminium in 2 M HCl. This is probably due to the constant attack of the chloride ions on the aluminium. Introduction of the compounds into the corrodent (HCl solution) depicts a progressive decreased deflection in hydrogen gas evolution reaction. This observation is in agreement with the views held by Onuchukwu [24] when he studied the variation of volume of hydrogen evolved with time of exposure of aluminium in 0.15 M KOH.

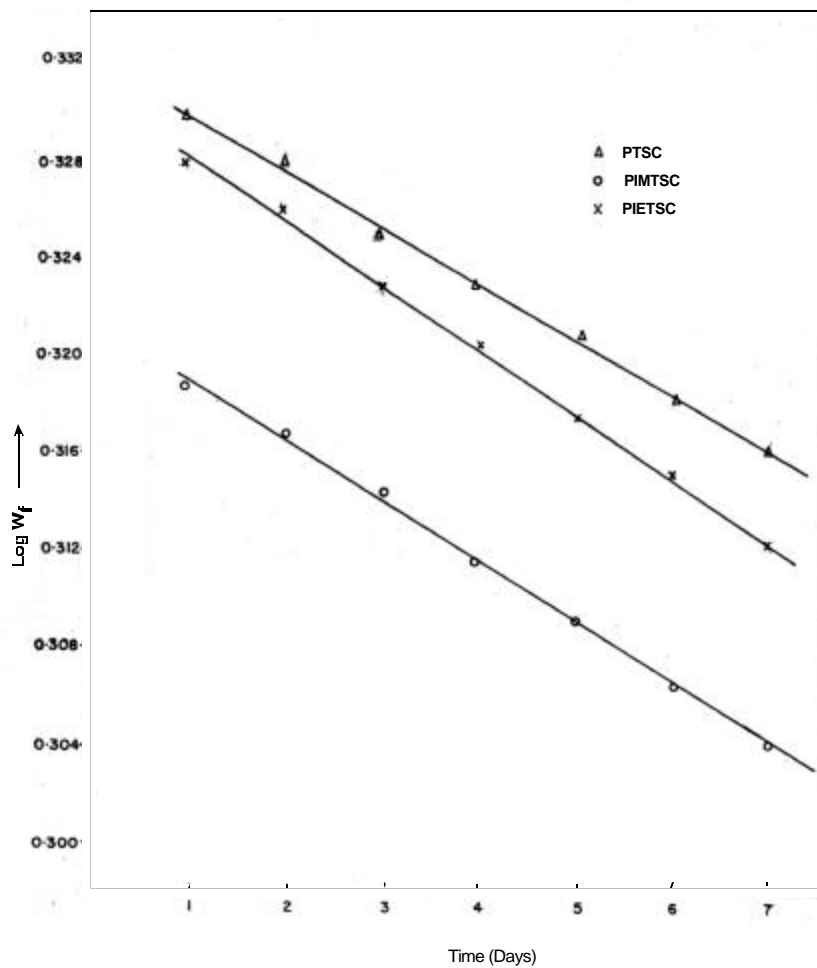


Figure 6. Variation of $\log W_f$ with time for aluminium in 0.1 M HCl solution containing 5×10^{-4} M of the compounds.

Application of the principles of chemical kinetics to the weight loss results

The kinetics of the corrosion process acquire the character of a diffusion process, in which at higher temperatures, the quantity of inhibitor present at the metal surface is lower than at lower temperatures. Figure 6 shows the variation of $\log W_f$ (W_f means final weight loss) with time for aluminium in 0.1 M HCl solution containing 5×10^{-4} M of the compounds at 30 °C. A linear variation was observed which confirms a first order reaction kinetics with respect to aluminium in 0.1 M HCl solution.

Tables 1-3 give the kinetic data obtained in the presence of PTSC, PIMTSC and PIETSC, respectively. From all the tables, rate constants and half life ($t_{1/2}$) show a general increase with increased temperature. Similar trend in kinetic data has been reported previously by other authors [17, 18]. The tables also show that $t_{1/2}$ is higher at higher concentrations which support that the compounds inhibit the corrosion of aluminium to an appreciable extent at higher concentrations.

CONCLUSION

The compounds used as inhibitors (PTSC, PIMTSC and PIETSC) retard the acid corrosion of aluminium to a remarkable degree being physically adsorbed onto the metal surface. The inhibition efficiency (% I) increases with increase in inhibitor concentration and decreases with increase in temperature.

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