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Corrosion inhibition of aluminum in hydrochloric acid by 2-acetylpyridine thiosemicarbazone derivatives.

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ABSTRACT

The corrosion inhibition of aluminum in HCl medium by 2-acetylpyridine-(4-methyl-iso-methylthiosemicarbazone) (AMSM)and 2-acetylpyridine-(4-methyl-iso-ethylthiosemicarbazone) (AMSE) has been studied using weight loss and hydrogen evolution techniques. The inhibition efficiency of the compounds was tested for five concentrations in the range 1 x 10^{-5} to 5 x 10^{-4}M. The AMSM exhibited a higher inhibition efficiency than AMSE. Generally, inhibition was observed to decrease with decreasing temperature. A first order type of mechanism has been deduced from the kinetic treatment of the results. The process of inhibition was attributed to physisorption. The difference in the inhibition behaviour of the two compounds is explained in terms of the difference in their molecular structures.

Keywords: Inhibition, thiosemicarbazone derivatives, aluminum, corrosion.

INTRODUCTION

Aluminum alloys enjoy a wide range of commercial usage due to their numerous desirable properties such as lightness, high thermal conductivity and reflecting surfaces (Ekpe *et al*., 1997). The greatly expanded industrial applications of aluminum alloys with respect to their surface properties have been reported by Wernick (1964). However, the inherent problem of the corrosion of aluminum alloys which renders them quite unsuitable under certain conditions is a matter of great concern. Several N-and S- containing compounds have been reported as corrosion inhibitors for aluminum (Babaqi *et al*., 1989; Peterside, 1994; Onuchukwu, 1990). In most of the work available in the literature on aluminum corrosion, scientists have tried to determine the mechanism of corrosion inhibition as well as compare the inhibitive actions of certain inhibitors.

In continuation of the search for efficient corrosion inhibitors for aluminum in hydrochloric acid, the inhibition effects of 2-acetylpyridine- (4-methyl-iso-methylthiosemicarbazone) (AMSM) and 2-acetylpyridine-(4-methyl-iso-ethylthiosemicarbazone) (AMSE) are reported. The inhibition efficiency (%) of the thiosemicarbazones were obtained from a known relation (Ita and Offiong, 1997a) :

$$\text{I. E. } (\%) = [(X_o - X_1) / X_o] \times 100 \quad \ldots (1)$$

where X_o and X_1 are the weight loss (or hydrogen evolution) in the absence and the presence of inhibitors respectively.

EXPERIMENTAL

Weight loss and hydrogen evolution corrosion test methods were employed for this study.

Materials preparation

The sheets of aluminum alloy of type AA3003 and purity 98.5% used for this study were purchased from System Metals Industries Limited, Calabar, Nigeria. The sheet was mechanically cut into 5 x 4cm coupons. Holes were made at the centre of each coupon (one hole per coupon) for the insertion of hooks. The coupons were examined for lack of edge roughness, which could influence the corrosion process. These coupons were used as supplied without further polishing. However, surface treatment of the coupons involved degreasing in absolute ethanol and the degreased coupons dried at 80^{o}C for 30 min in a thermostated electric oven and stored in a moisture-free desiccator prior to use (Talati, 1986).

The inhibitors used were 2-acetylpyridine-(4-methyl-iso-methylthiosemicarbazone) (AMSM) and 2-acetylpyridine-(4-methyl-isoethylthiosemicarbazone) (AMSE). These inhibitors were each recrystallized twice from absolute ethanol and dried in air. Inhibitor concentrations of 1 x 10^{-5}M to 5 x 10^{-4}M were prepared in 0.1M HCl solution and used at 30 and 40^{o}C. The prepared inhibitor solutions were used for all measurements.

Weight loss determination

A set of 250ml beakers separately contained 0.005, 0.01, 0.05, 0.1 and 0.5M HCl solutions respectively. Previously weighed Al coupons were each immersed in each test solution with the help of glass rods and glass hooks. Each test was carried out at 30^o and 40^{o}C.

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The coupons were retrieved from their corrodent solutions at 24h intervals progressively for a period of 7 days, washed by immersion in concentrated nitric acid (S.G. 1.42) scrubbed with bristle brush in distilled water, air dried and reweighed (Ekpe *et al*., 1997). The difference in weight was taken as the weight loss (g).

The second segment of the work involved the introduction of the inhibitors into two sets of five 250ml beakers containing 0.1M HCl and kept at 30 and 40^{o}C respectively. The beakers then contained 1 x 10^{-5}, 2 x 10^{-5}, 5 x 10^{-5}, 1 x 10^{-4} and 5 x 10^{-4}M inhibitor concentrations respectively and the previously weighed Al coupons. At 24h intervals, these coupons were retrieved from their solutions, washed as before and weighed. The difference in weight was taken as the weight loss.

Hydrogen evolution measurements

Hydrogen evolution measurements were carried out via the gasometric assembly. This assembly has been reported by Onuchukwu (1990), Ita and Offiong (1997a). The reaction vessel (two necked flask) was connected to a burette via a delivery tube. The corrodent (2M HCl) was introduced into the vessel and initial volume of air in the burette was recorded. Thereafter, two aluminum coupons were dropped into the corrodent and the flask quickly closed. All possible areas of leakages were adequately sealed with the help of petroleum jelly. The volume of H_2 gas evolved from the corrosion reaction was monitored by the volume change in the level of the paraffin oil in the graduated burette. The change in volume was recorded every minute for a period of 30 min.

In another experiment, freshly washed Al alloy coupons were immersed in 200ml of 2M HCl solution containing the inhibitors separately and the volume of H_2 gas evolved measured. This experiment was performed at different concentrations (1 x 10^{-5}, 2 x 10^{-5}, 5 x 10^{-5}, 1 x 10^{-4} and 5 x 10^{-4}M) of inhibitors.

RESULTS AND DISCUSSION

Effect of corrodent concentrations and temperature on aluminum corrosion

The influence of corrodent concentration on aluminum corrosion is shown in Figure 1. It is observed that the weight loss of aluminum increases with increased concentration of HCl. Weight loss recorded at 0.5M HCl solution at the end of 7 days was fifteen times greater than that at 0.005M HCl solution. This observation could be attributed to increase in concentration of active components involved in the corrosion reaction as well as the amphoteric nature of the aluminum which renders it non-resistant to attack by strong acids (Ekpe *et al*., 1997). Figure 2 is a representative plot of weight loss against time for aluminum coupons in 0.1M HCl solution without inhibitor at 30 and 40^{o}C. Similar plots were obtained for the corrosion of aluminum in 0.5M, 0.01M and 0.005M HCl solutions. For all the plots there appeared to be a general increase in weight loss as the temperature increased. This is not surprising, since the rate of a chemical reaction increases with increasing temperature. The dependence of the rate of a chemical reaction on the temperature could be depicted from the Arrhenius equation:

$$k = A \exp(-Ea/RT) \quad \ldots (2)$$

where; k is the rate constant, A is the Arrhenius frequency factor, Ea is the activation energy, R is the universal gas constant and T the temperature.

A generalization regarding the effect of temperature on reaction rate is that for most reactions, rate usually doubles for every 10^{o} rise in temperature, since the reactant molecules overcome the energy barrier more readily.

Effect of inhibitor concentration on inhibition efficiency

Figures 3 to 5 show that the various compounds studied (AMSM and AMSE) actually inhibit the acid corrosion of aluminum to a remarkable extent.

Figure 5 also shows that inhibition efficiency increases with increased inhibitor concentration. A very significant result obtained from Fig. 5 is the order of effectiveness of the inhibitors obtained as AMSM >AMSE at all temperatures studied. This trend of inhibition effectiveness is also confirmed from the hydrogen evolution measurements (Fig. 6) studied at very high corrodent concentration (2M HCl) to assess the inhibitor effects.

The low values of inhibition efficiency obtained at 2M HCl solution (Fig. 6) than at 0.1M HCl solution (Fig. 5) is physically reasonable and signifies the important role of the corrodent concentrations on inhibition efficiency. At 2M HCl solution, it is expected that the effect of dissolution could exceed that of adsorption of the inhibitors on the aluminum because of the high chloride ion concentration leading to a reduction in inhibition efficiency when compared with 0.1M HCl solution.

Application of the principle of chemical kinetics to the present result

Figures 1, 3 and 4 show that the corrosion of aluminum in HCl solutions without inhibitor and in the presence of inhibitor is a heterogenous one. This assertion is made from the non-uniformity of the plots. It is on this basis that the kinetic analysis of the present data became necessary. When logΔW was plotted against time (in days) at temperatures of 30 and 40^{o}C, a linear variation was observed, which confirms a first order reaction kinetics with respect to aluminum in HCl solutions. Typical linear plots are shown in Figures 7 and 8 at 30^{o}C.

Tables 1 and 2 give the kinetic data obtained in the presence of AMSM and AMSE, respectively. The rate constants at 30^{o}C (K_{30}) and 40^{o}C (K_{40}) enabled us to calculate the activation energy of the system using the equations:

$$\text{In}\,(k_{40}/k_{30}) = Ea / R\,(1/T_1 - 1/T_2) \quad \ldots (3)$$

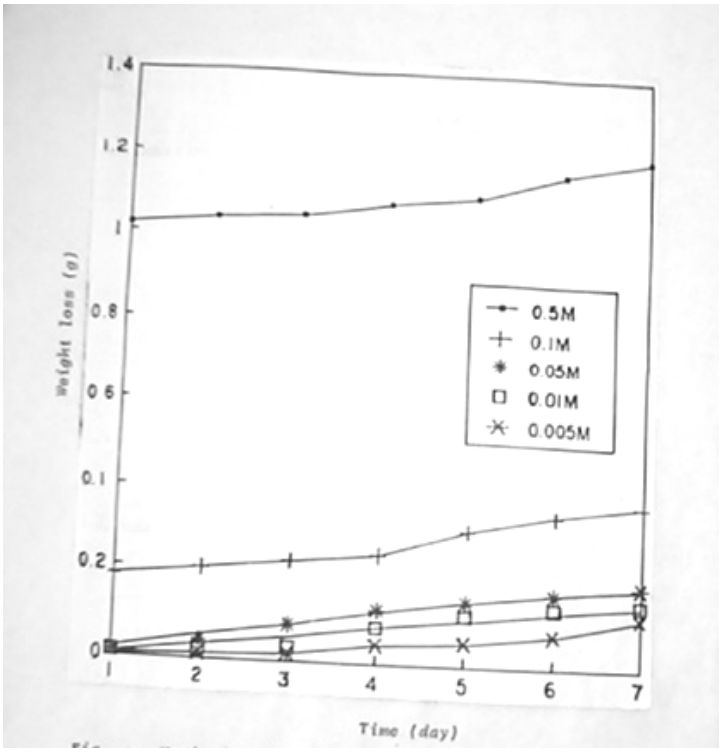

Fig. 1. Variation of weight loss (g) with time (day) for aluminium coupons in different concentrations of HCl solutions without inhibitor at 30^{o}C.

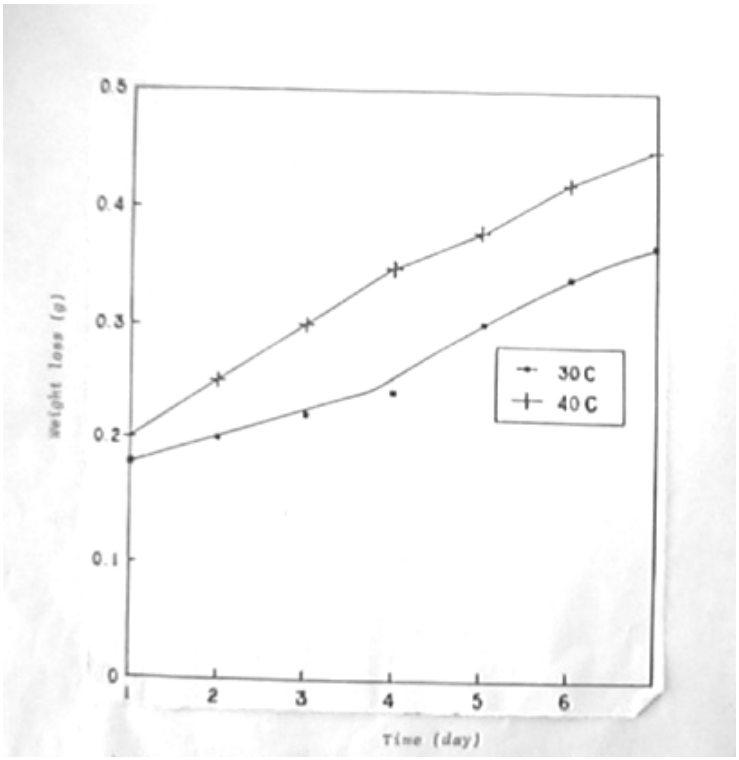

Fig. 2. Variation of weight loss (g) with time (day) for aluminium coupons in 0.1M HCl solutions at 30^{o}C without inhibitor.

and

$$E_1\ (KJ/mol^{-1}) = E_2\ (KJmol^{-1}) - E_3\ (KJmol^{-1}) \quad \ldots (4)$$

where: E_1 is the activation energy of a particular inhibitor, E_2 is the activation energy of the metal-corrodent-inhibitor system and E_3 is the activation energy of the metal-corrodent system without inhibitor. The rate constants, k_{30} and k_{40} without inhibitor are 0.0691 day^{-1} and 0.0824 day^{-1} respectively while 13.89 KJmol^{-1} is obtained as the average activation energy at 30 and 40^{o}C and 0.1M HCl solution. Also 11.97 KJmol^{-1} and 1.33 KJmol^{-1} were obtained as the average activation energies of AMSM and AMSE respectively at 30 and 40^{o}C in 0.1M HCl solution.

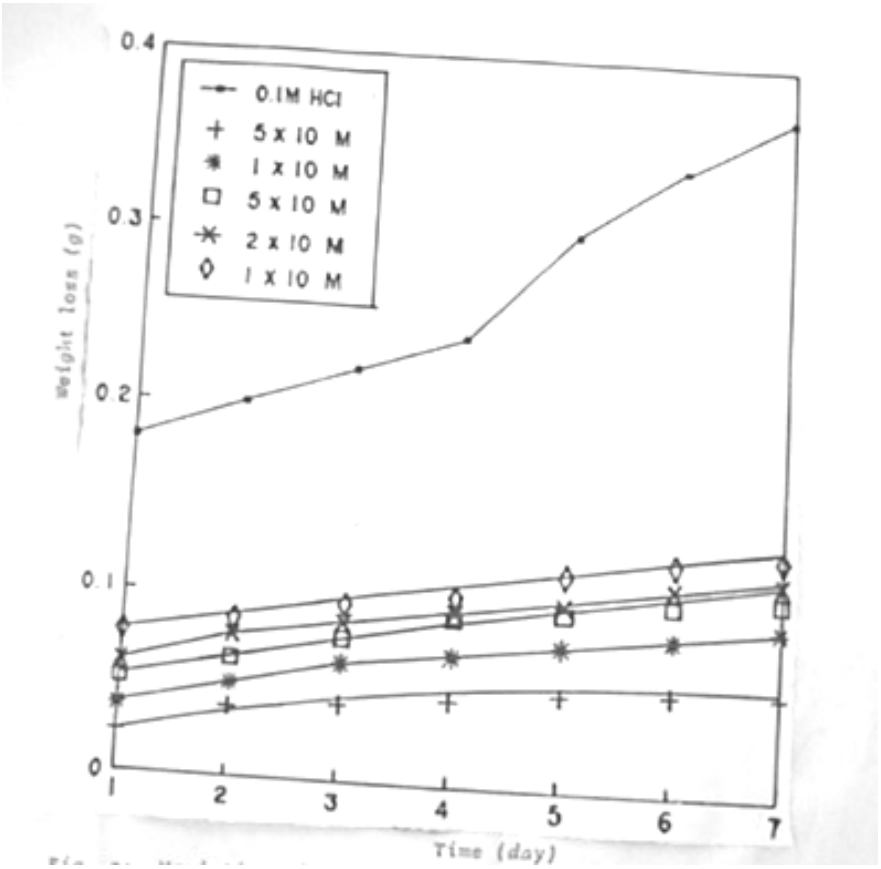

Fig. 3. Variation of weight loss (g) with time for aluminium coupons in 0.1M HCl solution containing different concentrations of AMSM at 30°C.

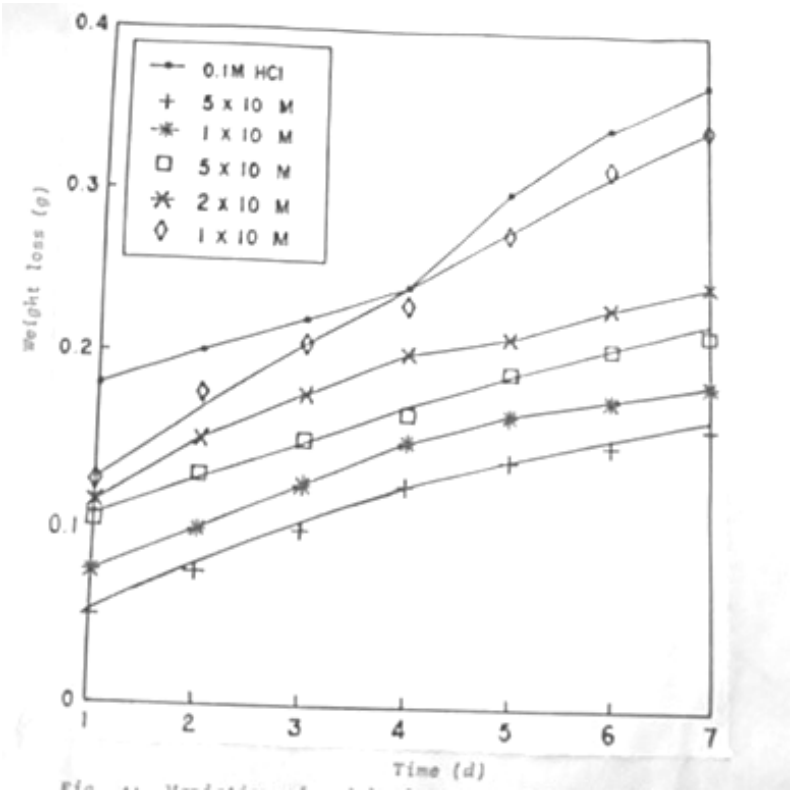

Fig. 4. Variation of weight loss (g) with time (day) for aluminium coupons in 0.1M HCl solution containing different concentrations of AMSE at 30°C.

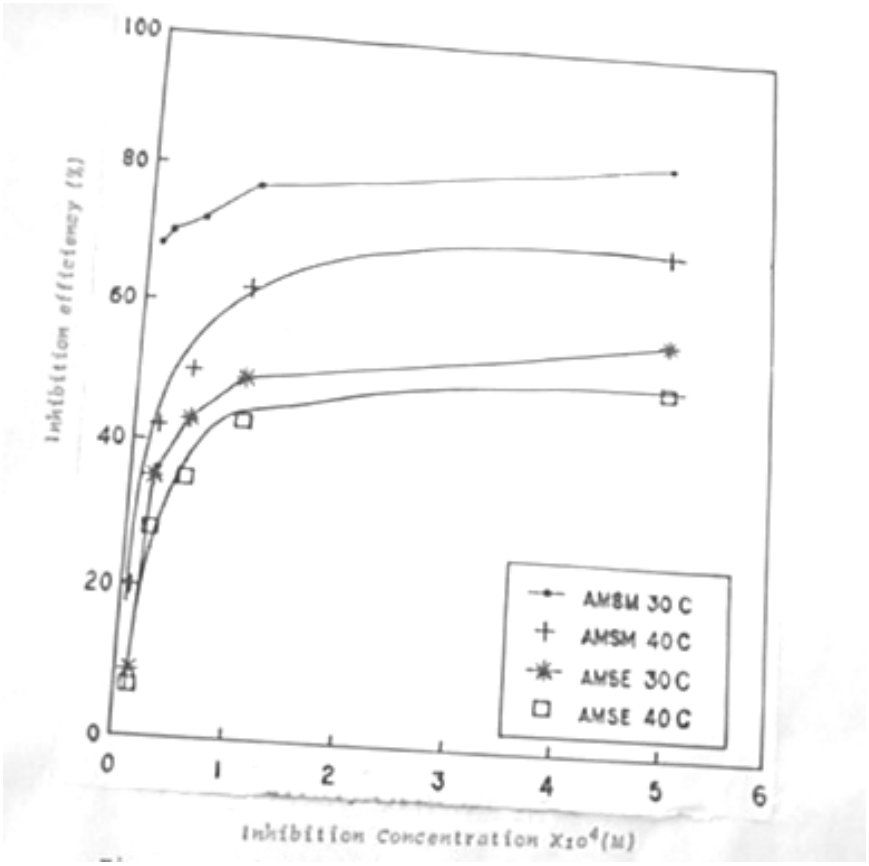

Fig. 5. Variation of inhibitor efficiency (%) with inhibitor concentration (M) for aluminium coupons in 0.1M HCl solution containing AMSM and AMSE inhibitors at 30°C.

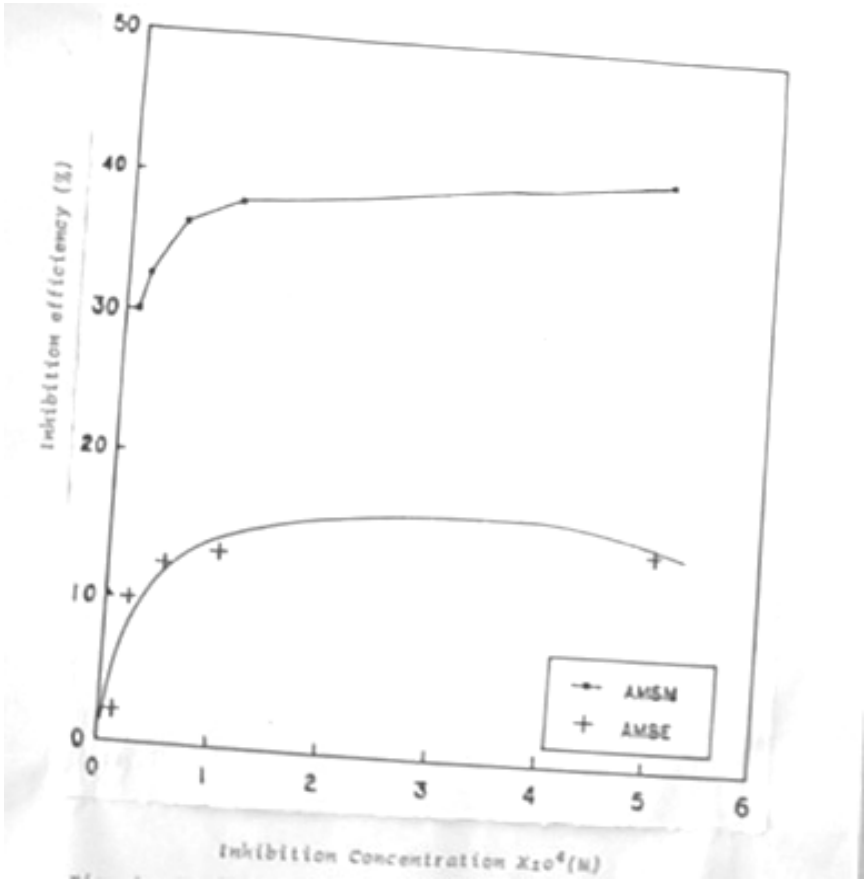

Fig. 6. Variation of inhibition efficiency (%) with inhibitor concentration (M) for aluminium coupons in 8M HCl solution containing AMSM and AMSE via hydrogen evolution measurement.

Table 1. Kinetic data for Al in 0.1M HCl solution containing AMSM via weight loss measurement.

Inhibitor Conc. (x 10^4M)	K_{30} (day^{-1})	K_{40} (day^{-1})	Activation energy ($KJmol^{-1}$)	Average activation energy ($KJmol^{-1}$)
0.1	0.114	0.1334	0.31	
0.2	0.1152	0.1522	8.07	
0.5	0.1105	0.1467	8.41	11.97
1.0	0.0518	0.0729	13.05	
5.0	0.1520	0.2652	30.00	

Table 2. Kinetic data for Al in 0.1M HCl solution containing AMSE via weight loss measurement.

Inhibitor Conc. (x 10^4M)	K_{30} (day^{-1})	K_{40} (day^{-1})	Activation energy ($KJmol^{-1}$)	Average activation energy ($KJmol^{-1}$)
0.1	0.1890	0.2263	0.31	
0.2	0.1303	0.1563	0.32	
0.5	0.1468	0.1758	0.34	1.33
1.0	0.1689	0.2045	1.19	
5.0	0.2591	0.3272	4.50	

Comparison of corrosion inhibition behaviour of the inhibitors studied

Figures 5 and 6 reveal that AMSM exhibits a better corrosion inhibition tendency than AMSE. The highest inhibition efficiencies were exhibited by AMSM. These are 83% and 41% from weight loss and hydrogen evolution measurements respectively. AMSE exhibited 57% and 15% from weight loss and hydrogen evolution respectively, at 5.0 x 10^{-4}M inhibitor concentration at 30°C. At 40°C low values of inhibition efficiencies are recorded for all the inhibitors, signifying that the compounds are all physically adsorbed on the aluminum coupons for the inhibition to be effective. Figure 9 is the plot of logarithm of inhibition efficiency against logarithm of inhibitor concentration. Similar plots have been reported by Talati and Modi (1986) and Ita and Offiong (1997a). A linear variation observed reveals that the compounds adsorb following Freundlich adsorption isotherm. Also the values of activation energy of 11.97 $KJmol^{-1}$ for AMSM and 1.33 $KJmol^{-1}$ for AMSE confirm the assertion that the inhibitors act by physical adsorption mechanism. This observation corroborates with those of Talati and Modi (1986) and Barrow (1993). These reports state that the heat of chemical adsorption should be greater than about 80$KJmol^{-1}$ and less than this value signifies a physical adsorption mechanism.

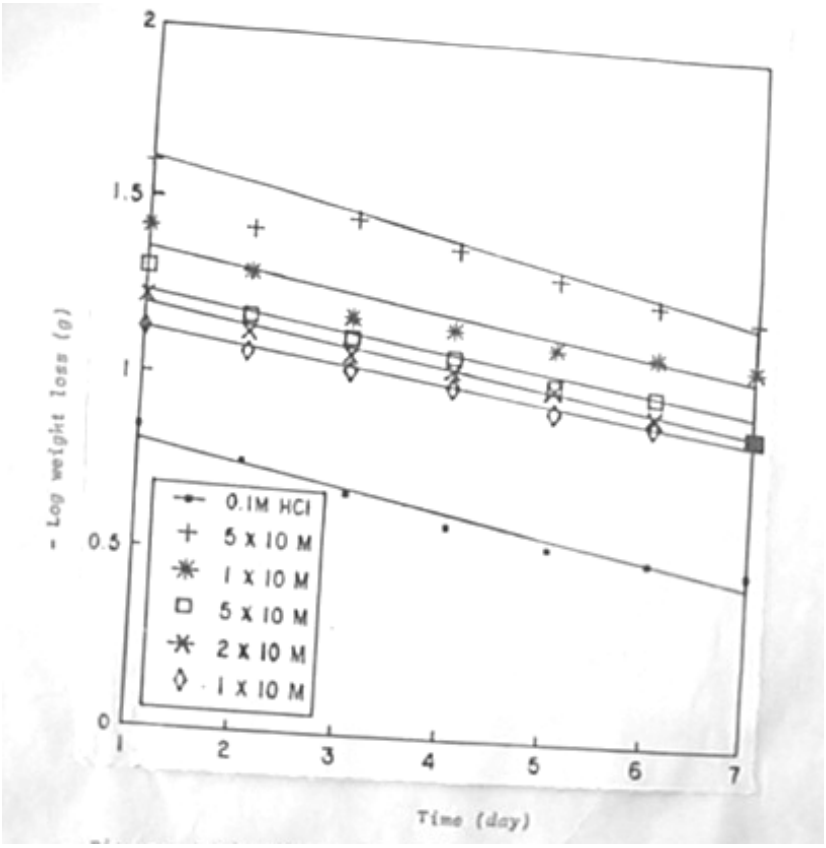

Fig. 7. Variation of –log AW (g) with time (day) for aluminium coupons in 0.1M HCl solution containing AMSM at 30°C.

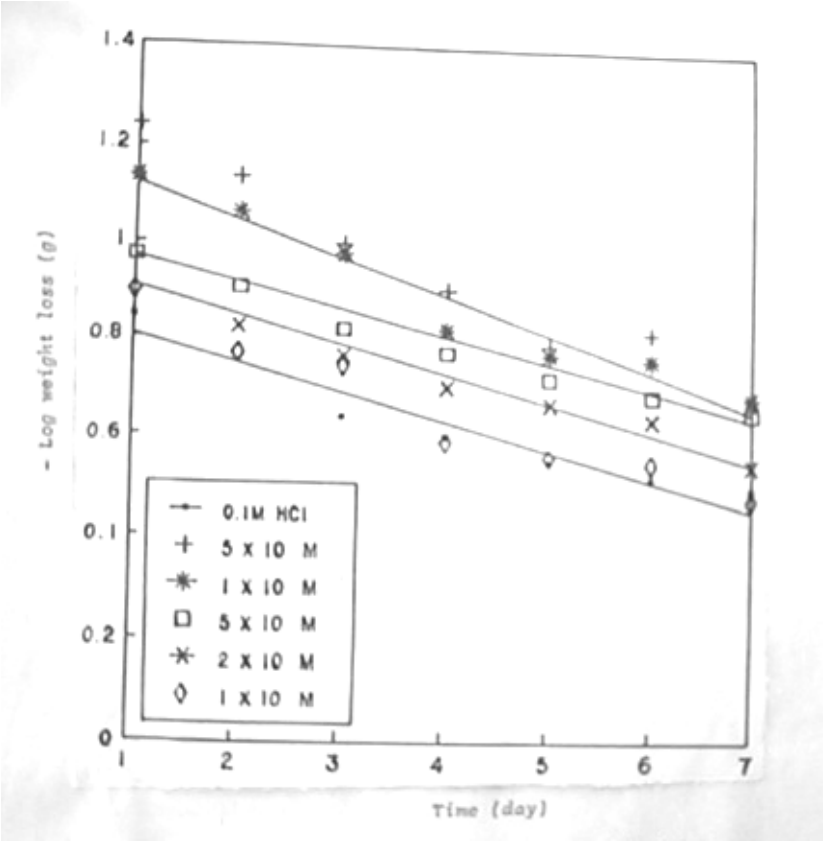

Fig. 8. Variation of –log AW (g) with time (day) for aluminium coupons in 0.1M HCl solution containing AMSE at 30°C.

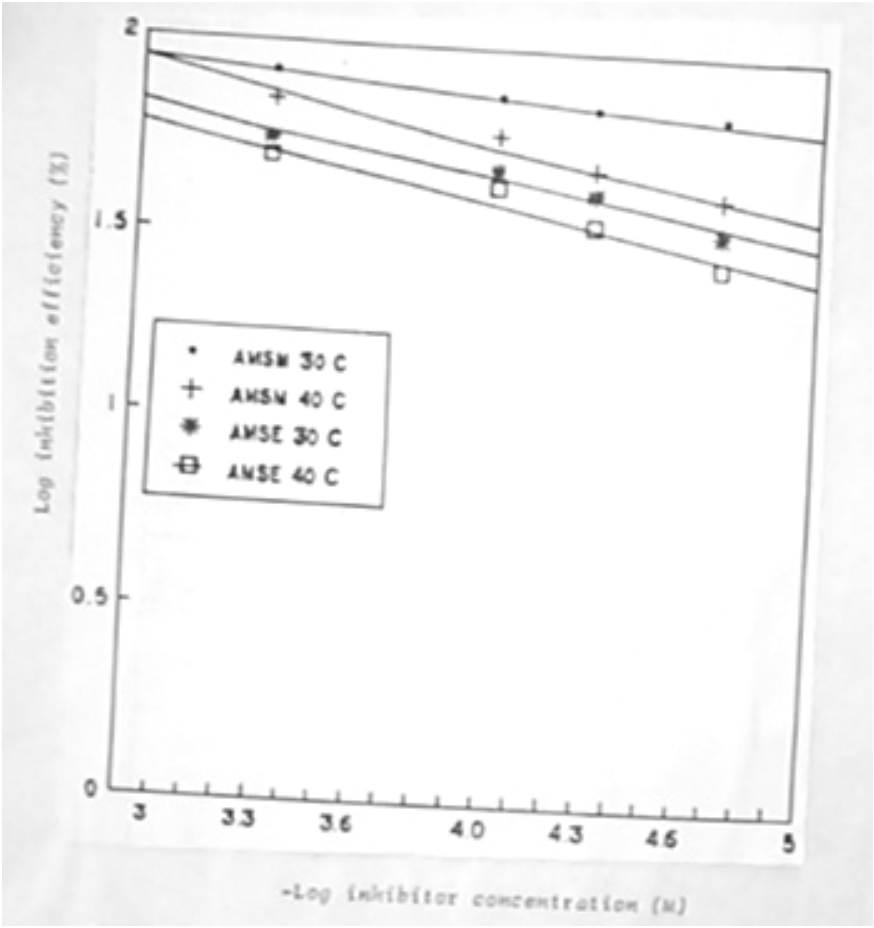

Fig. 9. Variation of log inhibitor efficiency (%) with –log inhibitor concentration for aluminium coupons in 0.1M HCl solution containing AMSM and AMSE at 30°C and 40°C.

Also, Ita and Offiong (1997b) have stated that for a chemical adsorption mechanism, the inhibition efficiency increases with increase in temperature while an increase in inhibition efficiency with decrease in temperature is suggestive of a physical adsorption mechanism. Since we have proposed physical adsorption mechanism for the present inhibitors, a multi-layer protective coverage is expected on the entire aluminum surface by the inhibitors for the inhibition to be effective. However, we observe that AMSE with a higher molecular weight (236) than AMSM (222) is less inhibitive than AMSM. This is probably due to the disruption of the multi-layer arising from over-loading of subsequent layers as a result of the high molecular weight of AMSE.

It is important to state that although we have proposed a physical adsorption mechanism for the inhibitors, this may not rule out completely the contributory effect of the structure (cyclic structure versus linear structure, electron donating or withdrawing groups), which in the present investigation plays very less significant role and is not considered sufficiently important for the purposes of our discussion. However, the influence of the structure would have been of interest in the case of chemical adsorption mechanism, where there is usually a dative link between the inhibitor and the metal (Ita and Offiong, 1997b).

CONCLUSION

The corrosion inhibitory actions of two inhibitors; AMSM and AMSE have been investigated for the first time in Al-HCl system. It is obse-rved that AMSM is a better inhibitor than AMSE for Al corrosion in HCl solutions at 30 and 40^{o}C. The inhibitors (AMSM and AMSE) inhibited the corrosion reaction probably being physically adsorbed onto the Al surface. The inhibition efficiency for a particular inhibitor increases with increasing inhibitor concentration and decreasing temperature.

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