INHIBITORY EFFECTS OF BENZOTRIAZOLE AND AMINE MIXTURES ON THE CORROSION OF GREY CAST IRON IN 0.1M POTASSIUM CHLORIDE SOLUTIONS

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Abstract
Inhibitory effects of triethanolamine [$(CH_2CH_2OH)_2$], triethylamine [$(CH_3CH_2)_3N$], triethanolamine [$(CH_2CH_2OH)_2$] + benzotriazole [$C_6H_5N_3$] and triethylamine [$(CH_3CH_2)_3N$] + benzotriazole [$C_6H_5N_3$] on the corrosion of grey cast iron in 0.1M potassium chloride (KCl) solutions have been investigated using the weight loss immersion and polarization methods. The inhibitive potentials of the four inhibitors were evaluated based on a determination of the corrosion rates in the presence and absence of the inhibitors at room temperature. The results obtained indicate that benzotriazole + triethanolamine and benzotriazole + triethylamine were observed to be more efficient than triethanolamine and triethylamine by providing corrosion inhibition at molar concentrations of 10^{-3}M and 10^{-2}M respectively. It was also observed that triethanolamine, triethylamine, triethanolamine + benzotriazole and triethylamine + benzotriazole showed considerable potentials with inhibition efficiencies of about 71.2%, 78.4%, 84.9% and 88.4% respectively in 0.1M potassium chloride solutions for grey cast iron. Polarization data revealed that benzotriazole is acting mainly on the anodic process rendering the passive film more stable and less susceptible to attack by the chloride ions. However, benzotriazole increased the pitting potential, but has a marginal influence on the behaviour of the grey cast iron under cathodic polarization. The results of this work are expected to be used to improve the corrosion resistance of cast iron for automobile and chemical industries in Nigeria.

Keywords: *corrosion, chloride, cast iron, inhibition efficiency, polarization.*

Introduction

Corrosion of grey cast irons has persistently become a major problem for instance as regards the use of copper, aluminum, stainless steels or titanium. There are some situations where the protection of cast iron against corrosion should be done. Two examples are engine cooling systems and cutting machines. In the former excessive accumulation of rust can lead to a decrease in efficiency of heat transfer and sometimes to blocking of the cooling systems. In cutting machines, corrosion of their various parts, including those made of cast iron, is generally unacceptable, the same applying to the work pieces.

Since the antifreeze mixtures used in engine cooling systems and many cutting fluids incorporate a considerable amount of water, inhibitors must be added in order to prevent corrosion of the various metals they contact with. This often leads to rather complex solutions because of the specific action of most inhibitors. Chromates protect most metals against corrosion, but they are highly toxic and react with the ethylene glycol incorporated in antifreeze mixtures, which prevents them from being used in either application. The other often used inorganic inhibitors also present problems that render them not very suitable for the same application. The alternative seems to reside in organic inhibitors. Carboxylates have been tested as corrosion inhibitors of steel cast iron and zinc and the results obtained with some of them are encouraging (Alagbe et al 2006, and Arkhipushkin et al, 2017). Nitrobenzoates are reported to have all-purpose protective properties similar to those of chromates (Recloux et al, 2017 Alagbe, 2016, and Tuan and Xianming, 2009).

In the present work the inhibitive properties of benzotriazole ($C_6H_5N_3$) towards cast iron have been investigated. Benzotriazole has usually been used to inhibit the corrosion of copper and its alloys, being more resistant to degradation by light and heat than mercaptobenzothyazole which is also an inhibitor for copper (Zhao et al, 2018 and Mansfeld et al, 2013).

Benzotriazole is a heterocyclic compound containing three nitrogen atoms, with the chemical formula $C_6H_5N_3$. This aromatic compound can be used as corrosion inhibitor (Robert, 2002).

The structure of benzotrizole consists of a benzene nucleus fused to a 1H-1, 2, 3-triazole ring.

The presence of a hydrogen atom bonded to one of the nitrogens confers to benzotriazole slight acid properties. Owing to its low solubility in neutral solutions benzotriazole has been added to the corrosive medium dissolved in either triethylamine $(CH_3CH_2)_3N$) or triethanolamine ($(CH_2CH_2OH)_3H$), making use of their alkaline properties. The use of triethylamine and triethanolamine had the objectives of investigating if the substitution of the alcohol group for one hydrogen atom in the radical had a significant influence on inhibition. The corrosive medium consisted of a 0.1M potassium chloride solution.

Materials and Method

Triethanolamine [$(CH_2CH_2OH0_2$], triethylamine [$(CH_3CH_2)_3N$], triethanolamine [$(CH_2CH_2OH0_2$] + benzotriazole [$C_6H_5N_3$] and triethylamine [$(CH_3CH_2)_3N$] + benzotriazole [$C_6H_5N_3$] were selected for this study, stored differently and varying concentration of these were prepared in 100ml of 0.1M potassium chloride solutions (0.1M KCl). The type of grey cast iron of Grade G3500, according to ASTM Designation A159, was used. Its chemical composition was: 3-5%C, 2.1%Si; 0.58%Mn; 0.1%P; 0.03%S. The hardness of the material was graphite flakes.

Weight loss test specimens were from the cast iron samples whose compositions are given above. The original cylindrical rods were cut into 160 short pieces having a cross section of 8mm and a gauge length of 40mm and their surfaces were given similar surfaces finishing using the same grades of emery papers 240, 320, 400 and 600grits for each sample. They were washed with distilled water, degreased in benzene and dried. Before weighing the specimens were left in the desiccators for 2days to allow the oxide film on the surface reach steady state. Afterward, the test specimens were weighed on FB 143 Mettle Toledo digital weighing balance.

Different concentrations (10^{-5} to 10^{-1}M) of inhibitors were prepared and added to the environments. Then another medium without any inhibitor was used for the control experiment. Specimens were weighed in turn and their original weights recorded. They were then totally immersed in 100ml of 0.1M potassium chloride solutions containing mixture of different concentrations of inhibitors. The specimens were removed after 48hours and weighed after cleaning off the corrosion products. The corrosion product formed on the surface of each specimen was removed by scrubbing under running water using fine emery paper. The specimens were then dried, re-weighed and the corrosion rates calculated in mils per year (mpy). Curves of corrosion rates in mils per year (mpy) versus the concentration of the inhibitors (M) were plotted for every medium. The inhibitor efficiency (P) in 0.1M potassium solutions was determined from the relationship.

$$P = 100\frac{(W1 - W2)}{W1} \quad (1)$$

Where, W1 and W2 are the corrosion rates in the absence and presence of the inhibitors respectively. All chemicals used were of analytical grade. The solutions were made from freshly distilled water. Initial pH readings of the inhibited solutions with concentration of amine (10^{-2}M) were measured and recorded in Table 1.

Table 1. Initial pH of the inhibited solutions

Inhibitor concentration: 10^{-2}M	pH
No inhibitor added	5.3
Triethanolamine	10.33
Triethylamine	12.40
Benzotriazole + Triethanolamine	8.36
Benzotriazole + Triethylamine	9.18

The cell for the polarization measurements consisted of three compartments separated by fitted glass discs to prevent the mixing of anolyte and catholyte. The reference electrode and working electrode compartments were separated by a lugging capillary to minimize the ohmic potential drop. A saturated calomel electrode and carbon electrode were used as reference and auxiliary electrodes respectively. The galvanostatic polarization studies were performed using a constant current source (DB – 300). The potentials during corrosion and polarization were measured using a digital multimeter (systronics – model 435) with an accuracy of $\pm$ 5MV. The experiments were repeated to confirm reproductively. The experiments were carried out for samples of grey cast iron at room temperature in the materials laboratory of department of Metallurgical Engineering, Kwara State polytechnic Ilorin, Nigeria.

Results and Discussion

Fig. 1 shows the relationship between the corrosion rates in (mpy) and the molar concentration of inhibitors for 0.1M potassium chloride solutions after 48hours of exposure. The curves of fig. 1 show that in chloride solution, benzotriazole + triethanolamine and benzotriazole + triethylamine cause a continuous decrease in corrosion rate with increase in molar concentration although rate of decrease was small initially, while triethanolamine and triethilamine cause an initial increase in corrosion rate with increase in molar concentration followed by a sharp drop in rate of corrosion after a critical inhibitor concentration. Benzotriazole + triethanolamine and benzotriazole + triethylamine provide inhibition at molar concentration of 10^{-3}M, while triethanolamine and triethylamine provide inhibition at molar concentration of 10^{-2}M in chloride medium. Examination of the curves shows that the inhibitive power in chloride solution in the order: triethanolamine < triethylamine < triethanolamine + benzotriazole < triethylamine + benzotriazole. The addition of benzotriazole accelerates the process of film formation on the corroding grey cast iron surface. Relationship between efficiency of inhibition and inhibitor concentrations in 0.1M potassium chloride solutions after 48hours of exposure is shown in fig. 2. This relation shows the increase in efficiency of the inhibitor on increasing its concentration of 10^{-2}M. However, triethanolamine, triethylamine, triethanolamine + benzotriazole and triethylamine + benzotriazole showed considerable potentials with inhibition efficiencies of about 71.2%, 78.4%, 84.9% and 88.4% respectively in 0.1M chloride solutions for grey cast iron. Apparently, these values correspond to the substitution of the alcohol group for one hydrogen atom in the radical which increases film stability by adsorbing on the corroding grey cast iron surface. The inhibition efficiencies of triethanolamine and triethylamine are adequate, though triethanolamine + benzotriazole and triethylamine + benzotriazole would be considered to be a marginally better inhibitors of grey cast iron corrosion in 0.1M chloride solutions.

The cathodic polarization curves shown in fig. 3 are those measure for grey cast iron in 0.1M potassium chloride solutions with various concentrations of triethanolamine, triethylamine, triethanolamine + benzotriazole and triethylamine + benzotriazole with current densities.

The amines curve a stifling of the cathodic curves in the whole range of potentials investigated. The degree of polarization decreases upon the addition of amines. The existence of a quasi-constant current region in some of these cathodic polarization curves was also observed. The presence of inhibitors concentration displacing the corrosion potential towards less negative values. Benzotriazole and amine mixtures content of the solution is however responsible for considerable changes in the currents reached in the plateau region as shown in fig. 3, where amine content only is seen to cause a consistent increase of the polarization current.

The anodic polarization curves shown in fig. 4 are those measured for grey cast irons in 0.1M potassium chloride solutions without and with various concentrations of triethanolamine, triethylamine, triethanolamine + benzotriazole and triethylamine + benzotriazole with current densities. In all the inhibited solutions, with the exception of those of triethanolamine, extensive passive potential regions were observed. The increases in current that occur towards the end of these curves was found to be associated with pitting corrosion. It is therefore appropriate to call the potential at which the current rises the pitting potential. The pitting potential increases in the order:

triethanolamine < triethylamine < triethanolamine + benzotriazole < triethylamine + benzotriazole

This sequence of the pitting potentials explains the reason that triethanolamine was the least effective substance in the weight loss experiments and why the solutions with benzotriazole have shown great inhibiting efficiency in similar experiments. It appears, therefore, that benzotriazole is acting mainly on the anodic process, rendering the passive film more stable and less susceptible to attack by the chloride ions. The role of benzotriazole in reducing the corrosion rate is different from that of the amines since it decreases the pH of the solution, whereas both triethanolamine and triethylamine increase it, as observed in Table 1. The slight acid properties of benzotriazole are due to the presence of an atom of hydrogen bonded to one of the nitrogen atoms. Benzotriazole is able to increase film stability by adsorbing on the surface by a process of electron donation, involving the pairs of one electron situated at the nitrogen atoms. The inhibition by the amines would occur by a similar process, but the replacement of $CH_3CH_2OH^-$ for $CH_3CH_3^-$ would cause a redistribution of the negative changes in the molecule with a displacement towards the oxygen atom. This would lead to a decrease in the electronic density near the N atom, thereby reducing the strength of adsorption and, therefore, causing a lower degree of inhibition.

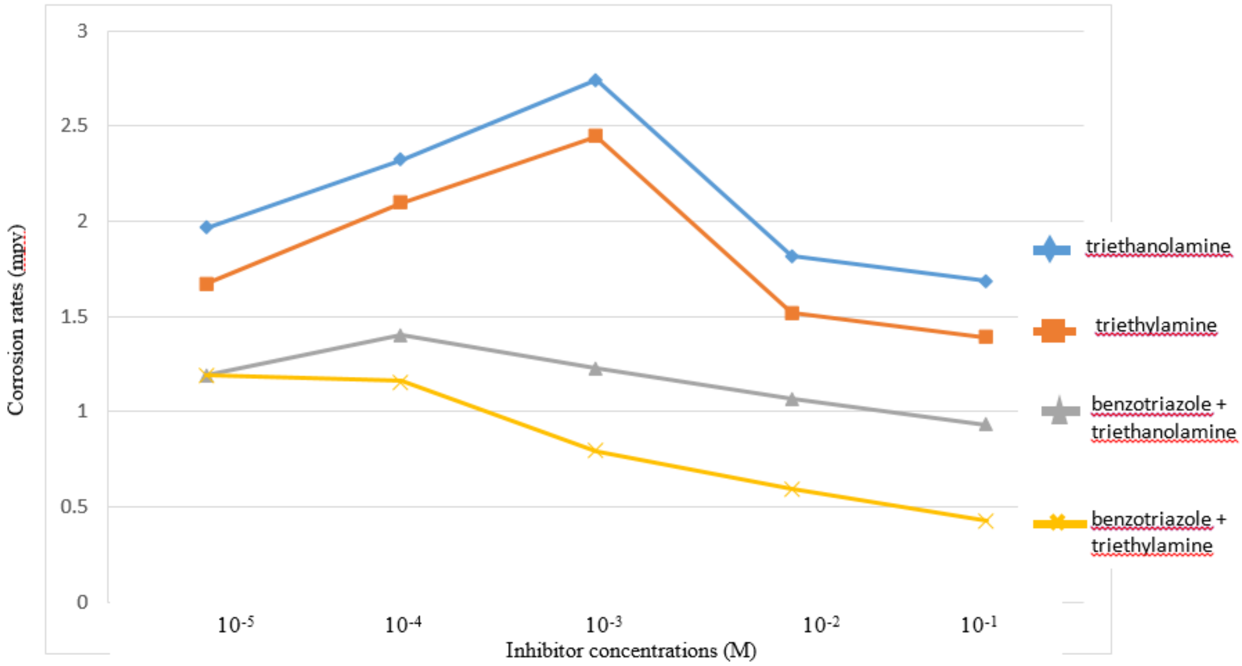

Fig. 1. Relationship between corrosion rates and inhibitor concentrations after 48hours of exposure in 0.1M KCl.

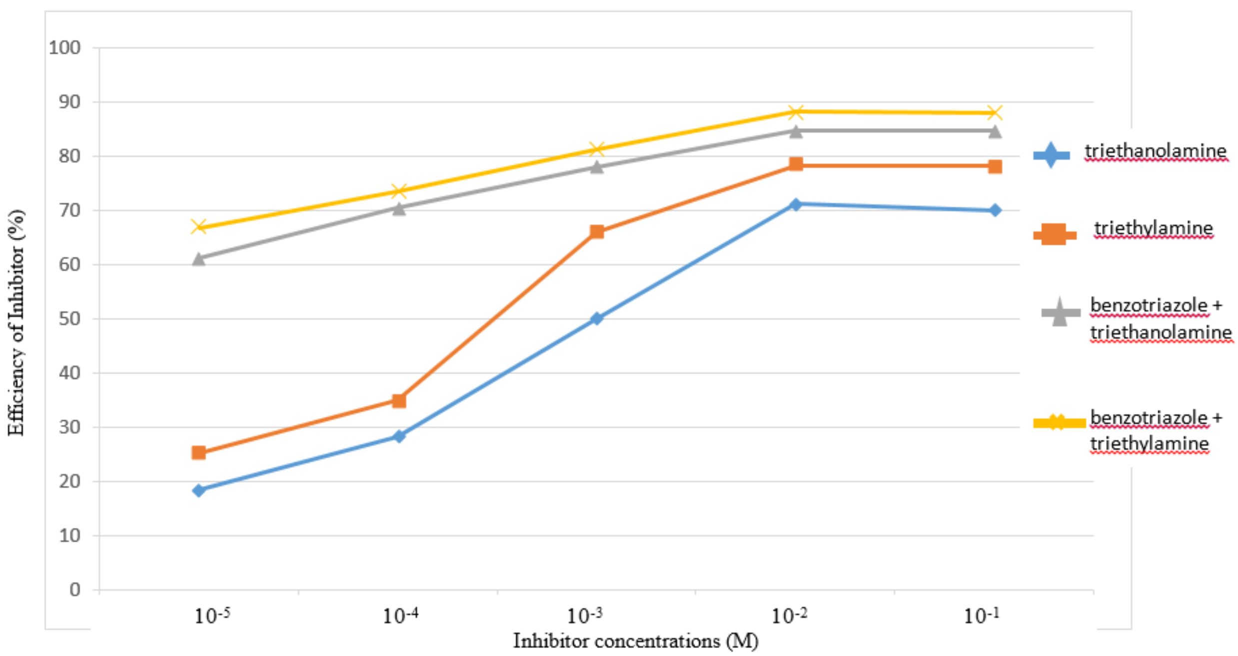

Fig. 2. Relationship between efficiency of inhibition and inhibitor

concentrations in 0.1M KCl after 48hours of exposure.

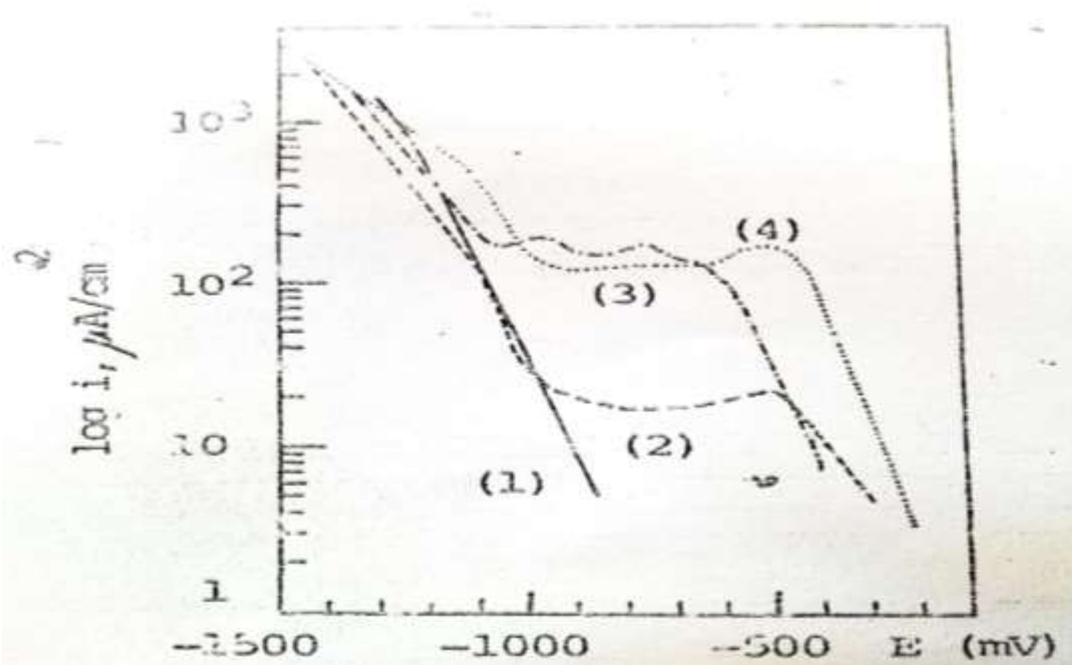

Fig. 3: Cathodic polarization for grey cast iron in 0.1M KCl containing 10^{-2}M inhibitors with:

(1) triethanolamine; (2) triethylamine; (3) benzotriazole + triethanolamine; and (4) benzotriazole + triethylamine

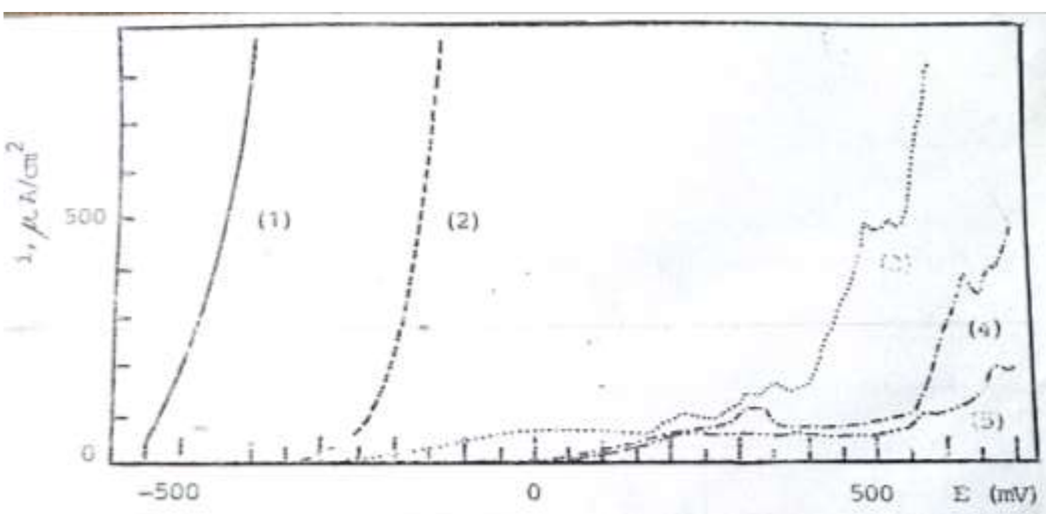

Fig. 4. Anodic polarization curves for grey cast iron in 0.1M KCl containing 10^{-2}M inhibitor with: (1) no inhibitor. (2) triethanolamine (3) triethylamine (4) benzotriazole + triethanolamine (5) benzotriazole + triethylamine

Conclusions

The main conclusions drawn from this investigation were:

- The corrosion of cast iron in 0.1M potassium chloride solution can be inhibited by benzotriazole and triethanolamine or triethylamine to varying degrees.
- The addition of benzotriazole accelerates the process of film formation on the corroding grey cast iron surface.
- The efficiency of inhibition in 0.1M potassium chloride solution increased in the following ranking order: triethanolamine, triethylamine, triethanolamine + benzotriazole and triethylamine + benzotriazole.
- The addition of benzoriazole to the amine solutions increased the pitting potential, but has a marginal influence on the behaviour of the grey cast iron under cathodic polarization.

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