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Inhibition effect of garlic extracts on the corrosion of alpha brass in nitric acid

***Cleophas A. Loto[1, 2] and Roland T. Loto[1]**

[1]*Department of Mechanical Engineering, Covenant University, Canaan Land, Ota, Nigeria*
[2]*Department of Chemical, Metallurgical and Materials Engineering, Tshwane University of Technology, Pretoria, South Africa*

ABSTRACT

The corrosion inhibition effect of allium sativum(garlic) extract as a 'green' inhibitor on α-brass in 0.5M HNO_3 was studied at ambient temperature. Weight loss and corrosion rate and potentiodynamic polarization measurement techniques were used for the experimental work. Potentiodynamic polarization measurement was performed using a potentiostat (Autolab PGSTAT 30 ECO CHIMIE) interfaced with a computer for data acquisition and analysis. The obtained results showed effective corrosioninhibition of the garlic extract on the test-specimens in the different concentrations of the test medium. There was increasing inhibition performance with increasing concentration of inhibitor. The best inhibition performance was achieved with the 100% (as extracted) garlic concentration. In 0.5M HNO_3, 100% garlic gave the optimal performance with weight loss of-0.021g, polarization resistance value of 6.88E+03 Ω, corrosion rate, CR, of 3.44E – 02 mm/yr and current density (Icorr) value of 3.74E-06 A/cm^2. Results of ba and bc indicate a mixed type inhibitor.

Key words: Corrosion, *Allium Sativum*, α-brass, inhibition, Nitric acid.

INTRODUCTION

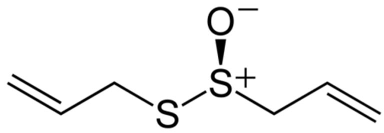
Alpha brass is a versatile metallic material that is widely used in manufacturing, marine and diverse areas of other industrial and engineering applications and for different purposes. Like any other metals/alloys, however, it is subject to adverse corrosive environmental degradation challenges in service that threatens its engineering performance and fulfillment. Chemical inhibitors have been used as a versatile means to mitigate this destructive phenomenon which can be disastrous and with economic and technological consequences. These are chemical compounds that are adsorbed on the metal surfaces to minimize, control and/or prevent corrosion destructive processes and reactions.

Recently, the use of plant extracts as inhibitors for the corrosion of metals/alloys, has gained very wide interest among researchers [1-12]. In addition, plant extracts have also been used as effective additives in electroplating processes [13-14]. In many cases, the corrosion inhibitive effect of some plants' extracts has been attributed to the presence of tannin in their chemical constituents. Also associated with the presence of tannin in the extracts is the bitter taste in the bark and /or leaves of the plants. Extracts of plants used as inhibitors are environment friendly.

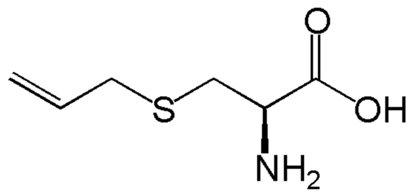
Extract of garlic, *Allium Sativum*, was investigated in this work. Garlic is of the Genus *Onions*; Class: *Equisetopsida* in the family of *Amaryllidaceae*. It is known to consist of calcium, Vitamin C, Vitamin B-6, Iron and Magnesium. It also contains protein, carbohydrates, potassium and sodium among many others. With the major chemical constituents, garlic contains 0.1-0.36% of a volatile oil. Garlic contains at least 33 sulphur compounds like aliin, allicin (diallylthiousulphinate or diallyl disulphide), ajoene, allylpropl, diallyl trisulphide, sallylcysteine, vinyldithiines, S-allylmercaptocystein, and others. Besides suphur compounds garlic contains 17 amino acids and their glycosides, arginine and others. Garlic also contains minerals such as selenium and enzymes like allinase, peroxidases, myrosinase, and others. Garlic contains a higher concentration of sulphur compounds than any other *Allium* species. The two major compounds in aged garlic, S-allylcysteine and S-allylmercapto-L-cysteine, had the highest radical scavenging activity. In addition, some organosulphur compounds derived from garlic, including S-allylcysteine, have been found to have significant medical value[15].

Garlic sulphur-containing compounds are classified as oil- and water-soluble compounds. Oil-soluble compounds include sulphides, such as diallyl sulphide (DAS), diallyl disulphide (DADS), diallyl trisulphide and allyl methyl trisulphide, dithiins, and ajoene. Water-soluble compounds include cysteine derivatives, such as S-allyl cysteine (SAC), S-allylmercaptocysteine (SAMC) and S-methyl cysteine, and gamma-glutamyl cysteine derivatives, all as previously mentioned above. [16].

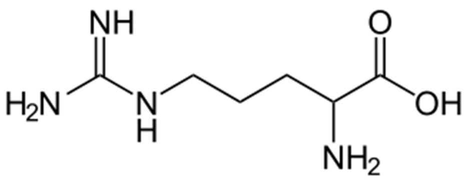
With the complex structural chemical compounds of the extract of garlic such as shown below (i-iii), a reasonable amount of exhibition of electrochemical corrosion activities of inhibition of the mild steel in the very corrosive acid environments used in this work is expected. Such a positive result is anticipated to have technologicaland economicbenefits.



(i) **Allicin** [17]



(ii) **S-allylcysteine** (SAC) [18]



(iii)**Arginine [19]**

MATERIALS AND METHODS

2.1. *Preparation of specimens*
The alpha brass specimen used as test specimens was obtained from a local metal market in Nigeria. It has a per cent nominal composition 70%Cu and 30%Zn. The cylindrical brass alloy sample was cut into average size of 20 mm x 20 mm coupons for weight loss measurements and 20 mm x 20 mm coupons for potentiostatic polarization measurements. Test samples used for the weight loss experiment were de-scaled with a wire brush, ground with various grades of emery paper and then polished to 6 μm,. They were further rinsed in distilled water to remove any corrosion products and then cleaned with acetone to degrease. The samples were fully immersed thereafter preventing further exposure to moisture in the atmosphere. Another set of samples for the corrosion polarization experiments were cleaned in the same manner as those for the weight loss experiment except that they were mounted in resin to ensure that only the surface of the samples were exposed to the corrosive medium. Before mounting, copper wire was spot welded to each of the samples.

2.2. *Preparation of Garlic (allium sativum) Extracts and Test Media*
The experiment was performed in 0.5M HNO_3 medium. The acid was of AnalaR grade. Garlic was obtained from the neighbourhood of the Covenant University, Ota, Nigeria. 1Kg of the garlic was chopped into pieces and soaked with 2.5 litres ethanol for 24 days. At the end of the soaking period, the chopped garlic was filtered to obtain a liquid solution of ethanol and garlic organic matter. The liquid was separated with the use of a rotary evaporator which extracted the ethanol from the liquid solution leaving behind the solution of garlic organic matter. The organic solution was stored in a refrigerator until it was used. The garlic extract (*allium sativum*) inhibitor test solutions were prepared in the percentage concentrations of 20, 40, 60, 80 and 100 respectively from the stock solution. This entailed taking 20 ml of the extract and 80 ml of the acidic medium to make 20% concentration. 100ml of the stock inhibitor solution was used as 100% *allium sativum* inhibitor concentration. The same procedure was followed to obtain 40%, 60% and 80% inhibitor concentrations. The HNO_3 medium was used for the preparation of percent concentrations of the extract inhibitors.

2.3. *Weight loss experiment*
Weighed test specimens were totally immersed in each of the test media contained in a 200 ml beaker for 20 days. Two test coupons were used for each test and the average weights used. Experiments were performed with 0.5M nitric acid test medium in which some had the *allium sativum* extract added. Test specimens were taken out of the test medium every 2 days, washed with distilled water, rinsed in methanol, air-dried, and re-weighed and then re-immersed in the test solution for continued tests during the whole experimental period. The plots of accumulated weight loss and of corresponding calculated corrosion rate versus exposure time are respectively presented in Figures 1 to 4. Corrosion rate was calculated from the formula in equation 1.

$$C. R. (mm/y) = 87.6 \times (W / DAT) \quad (1)$$

Where:
W = weight loss in milligrams
D = metal density in g /cm^3; A = exposed area of sample in cm^2
T = time of exposure of the in hours metal sample

The percentage inhibitor efficiency, P, for each of the corrosion rate results obtained for every experimental reading was calculated from the relationship:

$$P = 100[1 - W2/W1]$$

Where:W1 and W2 are, respectively, the corrosion rates in the absence and presence of the predetermined concentration of the *allium sativum* extract inhibitor. The results obtained are used to plot the curve(s) of % inhibition efficiency vs. exposure time (days), Figures 7 and 8.

2.4. Surface coverage
Surface coverage is defined as the number of adsorbed molecules on a surface divided by the number of molecules in a filled monolayer on that surface [20]. Surface coverage was calculated from the formula in equation 2.

$$¢ = (CR_{blank} – CR_{inh}) / CR_{blank} \quad (2)$$

Where:
¢ is surface coverage; $CR_{blank}$is corrosion rate without inhibitor, and CR_{inh} is the corrosion with inhibitor [21]

2.5. *Potentiostatic polarization experiments*
Potentiostatic polarization experiments were performed on the mounted specimens in turns by immersing them in each of the acid test media with and without garlic extract inhibitor. For test, 1 cm^2 surface area of the specimen was exposed to the test solution at room temperature. The experiments were performed using a polarization cell with a three – electrode system consisting of a reference electrode (silver chloride electrode– SCE), a working electrode (WE); and two carbon rod counter electrodes (CE). The potentiodynamic studies were made at a scan rate of 0.00166 V/s from −1.5 to +1.5 V and the corrosion currents were recorded. The experiments were conducted in different per cent concentrations of the HNO_3in garlic extract. The polarization cell was connected to a potentiostat

(Autolab PGSTAT 30 ECO CHIMIE) and interfaced with a computer for data acquisition and analysis. A scan rate of 1 mV/s was maintained throughout the experiment.

RESULTS AND DISCUSSION

Results from the experiments described above are presented below in this section in different subsections.

3.1 **Weight loss method**

3.1.1*Weight loss of brass in 0.5M HNO_3 + different concentrations of garlic extract*

The results obtained for the weight loss experiments performed with the different concentrations of the garlic extract used as the inhibitor in 0.5M HNO_3 are presented in Figure 1.

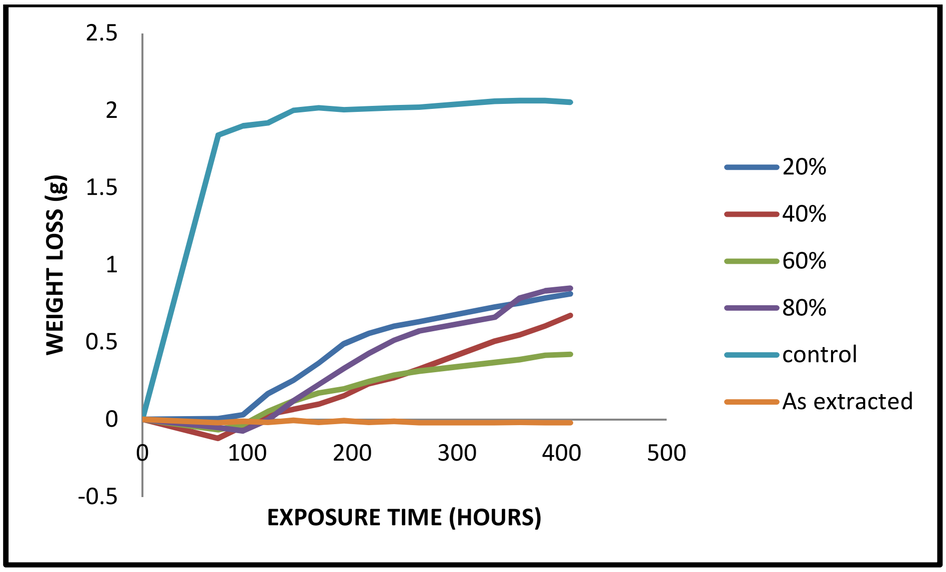


Figure 1: Plot of weight loss with exposure time for alpha brass specimen immersed in 0.5M HNO_3 in addition of different concentrations of garlic extract

The alpha brass test samples immersed in the 0.5M HNO_3 test medium with 20% inhibitor concentration lost the most weight within the 20 days duration of the experiment with a weight loss of 0.8129g as at 408 hours (17 days) of the experiment. The test sample immersed in the solution with 40% of inhibitor concentration showed improved corrosion inhibiting effect achieving a total weigtht loss of 0.6735g. The tests performed with the 60% and 80% extract inhibitor concentrations, similarly had improved corrosion inhibiting values with reduced weight loss of 0.4217g and 0.8494g as at the end of the experiment respectively. The tests performed with the as-received extract which was used as 100% inhibitor concentration gave an excellent result of corrosion inhibition. It achieved a negative corrosion weight loss value of -0.021g. This indicates absolute/perfect inhibition within the experimental conditions used. The value for the control experiment (without inhibitor addition) is 2.053g during the period of the experiment.

3.1.2. Corrosion rate of brass immersed in0.5M HNO_3+ different concentrations of garlic extract.

Results of corrosion rate obtained from the calculations of weight loss values for the specimen immersed in HNO3 plus different separate concentrations of garlic extract are presented in Figure 2.The highest corrosion rate of 8.543 mm/yr as at the end of the experiment, wasThe highest corrosion rate of 8.543 mm/yr as at the end of the experiment, was recorded with the test

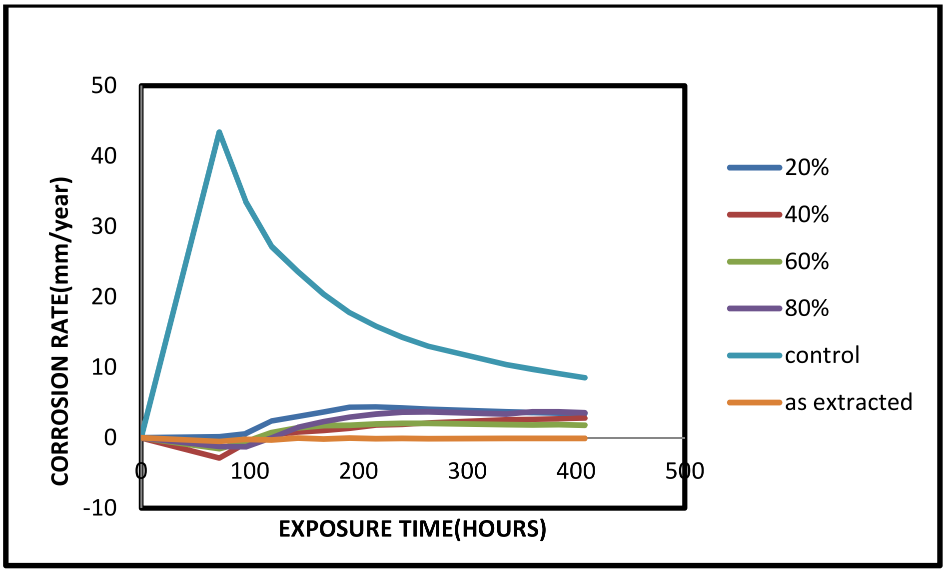


Figure 2: Plot of corrosion rate with exposure time for alpha brass immersed in 0.5M $HHNO_3$ in addition of different concentrations of garlic extract

specimen immersed in the test solution without added inhibitor (the control experiment). of 23.044 mm/yr. The corrosion inbition values for all the other inhibitor concentrations were very close indeed. These range between 3.680 and 3.5345 mm.yr for 20 and 80% inhibitor concentrations respectively. It only indicates the effectiveness, in general, of the garlic extract inhibitor concentrations in inhibiting the test specimen in the strong acidic medium. The extract used as 100%, that is, as- received extract, had the least corrosion rate with a corrosion rate value of-0.0898 mm/yr at the same period of the experiment.

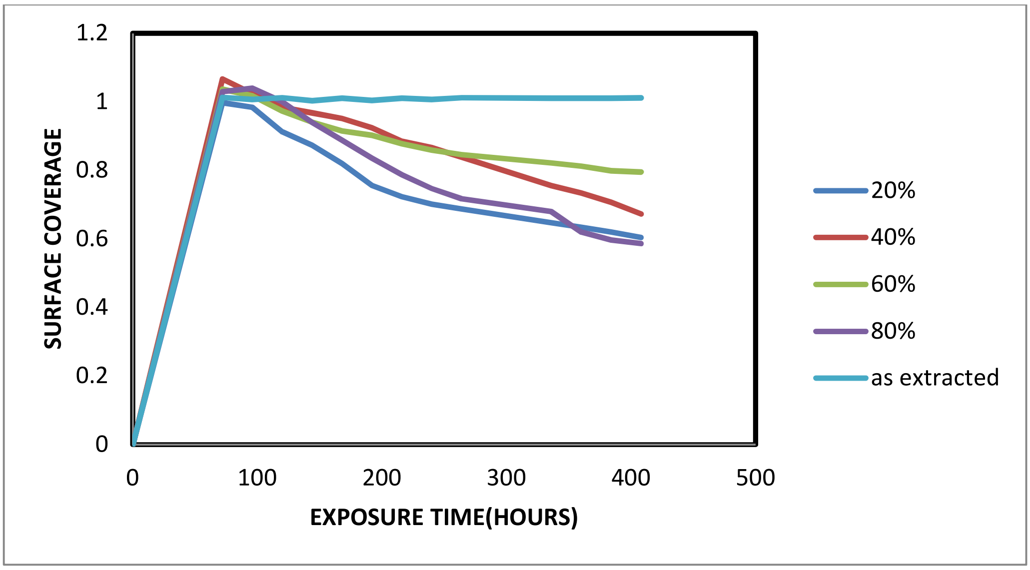


Figure 3. Plot of surface coverage with exposure time for brass immersed in 0.5M HNO_3 in addition of different concentrations of garlic extract

3.1.3. *Surface coverage of alpha brass immersed in 0.5M HNO_3 in different concentrations of garlic extract.*
Curves of the surface coverage of the garlic extract concentrations for corrosion inhibition of alpha brass in the acidic test media are presented in Figure 3. Except for the 100% extract, the surface coverage curves decreased progressively with the time of exposure. This was more pronounced with the inhibitor concentrations of 20, 40 and

80% respectively. The test with the 100% garlic extract maintained a very high and steady surface coverage value of 1.010 throughout the whole experiment indicating very effective protection and adsorption of the inhibiting molecules on the surface of the test electrode in the strong acidic concentration. On the other hand, the test with 20% extract inhibitor achieved a value of 0.647 of surface coverage as at 336 hours (14 days) of the experiment. This indicates lower comparative surface coverage performance. The active adsorbing molecules within the inhibitor concentration would have presumably been insufficient to be more effective. However, the overall trend was that of very fairly surface coverage achievement.

3.1.4. Inhibition efficiency of brass immersed in 0.5M HNO_3 in different concentrations of garlic extract

The results obtained for the corrosion inhibition efficiency of alpha brass immersed in 0.5M HNO3 test environment at different concentrations of *allium sativum* extract are presented in Figures 4. In general, the per cent inhibition efficiency decreased from the initial high values with the exposure time and thus becoming low at the latter part of the experiment. This could not be unconnected with the weakness of the corroding test medium caused by the contamination of the test environment by the corrosion products in the solution and the reduction in corrosion rate due to the consequent stifling action of the weak environment.

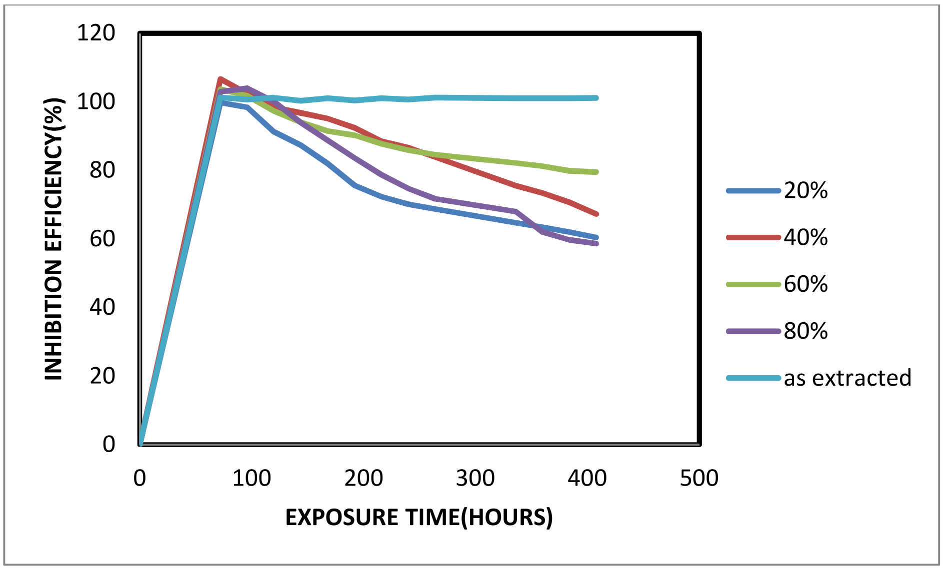


Figure 4:Percent inhibition efficiency of different concentrations of sativum allium extract addition with exposure time for brass immersed in 0.5M HNO3

Results presented in Figure 4, clearly show the additions of per cent garlic extracts of 20,40, 60, 80 and 100 recorded positive inhibition values. The inhibition efficiency values decreased with time to lower values achieving 61.95, 70.69, 79.88, 61.91 and 101.012 % for 20, 40, 60 ,80 and 100% inhibitor concentrations respectively.. The results obtained for all the inhibitor concentrations was an indication that the garlic extract was effective in exhibiting electrochemical activities of corrosion inhibition. This is one of the characteristics of the inhibitors. The available molecules in the extract (inhibitor) were considered adequate for the corrosion inhibition effectiveness in the strong acid environment. The highest inhibition efficiency (101.01%) was achieved with the 100% (as-extracted) inhibitor concentration. It thus provided excellent and effective protection throughout the experimental period.

3.2. PotentiodynamicPolarization

3.2.1. *Brass in HNO_3 with various concentrations of Allium Sativum(garlic) extract.*

Figures 5 to 9show the results obtained for the experiments performed in 0,5M HNO_3 test medium. Table 1 summarises the various parameters of electrochemical corrosion polarization results obtained for the various inhibitor concentrations during the experiments. The control experiment showed the highest corrosion magnitude as shown in the Table with corrosion rate of 6.49E+ 00 mm/yr; current density (Icorr), 7.05E-04 A/cm^2 and polarisation resistance, Rp, 3.65E + 01 Ω values respectively. The test with 20% inhibitor concentration recorded the highest corrosion values among the various inhibitor concentrations. This is shown by the current density, corrosion rate and polarization resistance values among other parameters. With an open corrosion potential (Ecorr) value of -0.428 V, the corrosion rate (CR) value was 4.28E + 00 mm/yr; the open corrosion potential (Ecorr) value was −0.44587 V while the corrosion polarisation resistance, Rp, value recorded was 6.17E + 01Ω and a value of 4.16E-04 A/cm^2 was recorded for corrosion current density (Icorr). All these results confirm the very active corrosion reactions at the test electrode/acid interface.

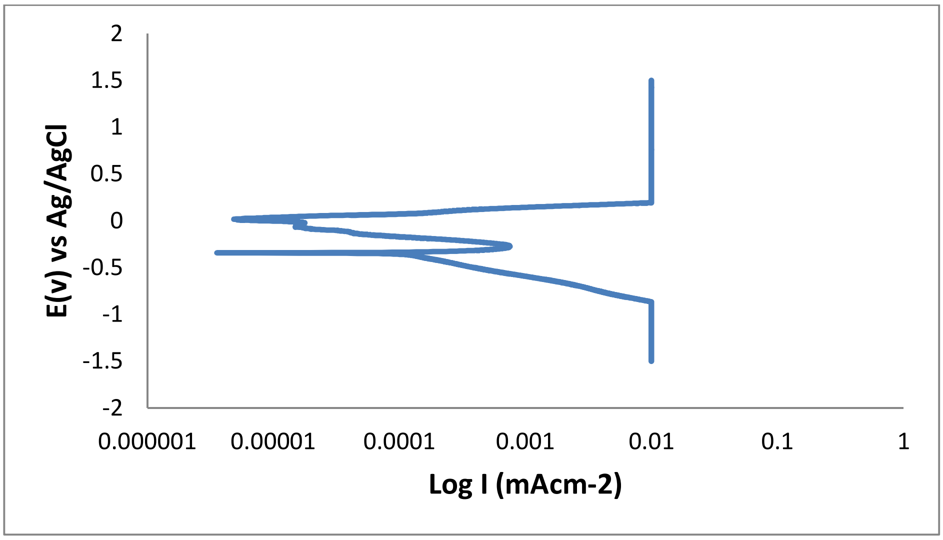


Figure 5:Polarization curve of brass in HNO_3 +20% garlic extract

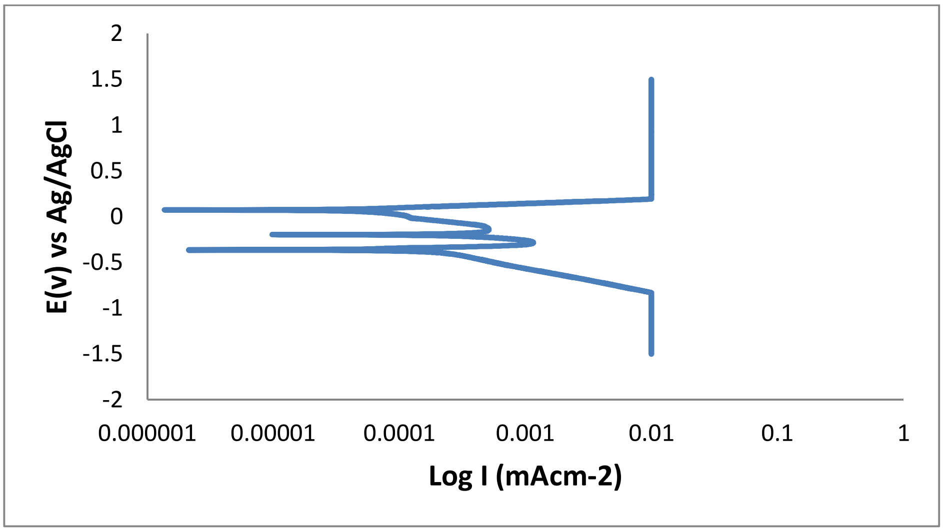


Figure 6: Polarization curve of brass in HNO_3 +40% garlic extract

From the Table 1 and also in Figures 5 to 9 that other results for 40, 60, 80 and 100% inhibitor concentrations showed very much improvement than that of 20%'s corrosion resistance//protection values. This is indicated by the decreasing corrosion rates, increasing polarisation resistance and decreasing current density, Icorr, values among other parameters. Corrosion rate values of 3.08E +00, 1.37E + 00 and 1.54E + 00 mm/yr were recorded for the extract concentrations of 40, 60, and 80% respectively. The corrosion potentiodynamic polarisation curve for the 100% (as extracted) inhibitor concentration is presented in Figure 9. The curve profile is very well defined. The Ecorr value, as obtained from Table 1, is -0.603 V; the current density, Icorr is 3.74E – 06 A/cm$_2$; the corrosion rate, CR, value is 3.44E – 02; a polarisation resistance, Rp, value of 6.88E + 03 Ω was recorded for the 100% inhibitor concentration. The corrosion inhibition at this concentration is very significant. The results obtained here are very much in agreement with the results obtained for the weight loss measurements. The results, in general, showed appreciable though variable corrosion inhibition of the brass specimen with all the extract concentrations used.The values of the Tafel slope (baand bc) indicate that the extract inhibits both cathodic and anodic reactions. It can therefore be described as exhibiting a mixed corrosion inhibition.

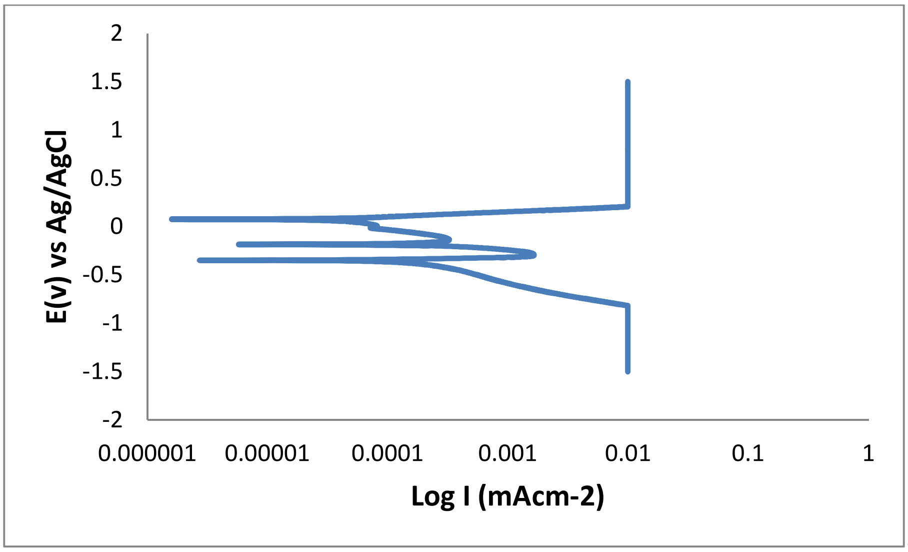


Figure 7:Polarization curve of brass in HNO_3 +60% garlic extract

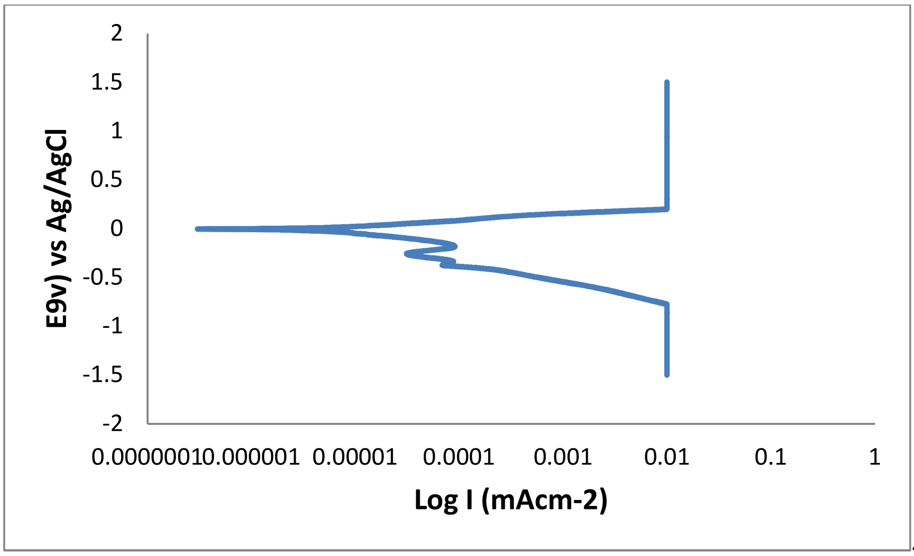


Figure 8:Polarization curve of brass in HNO_3 +80% garlic extract

Table 1: Polarization results for the specimen immersed in HNO_3 using different concentrations of per cent garlic extract

Inhibitor concentration	Ba (V/dec)	Bc (V/dec)	Ecorr, Calc (V)	Icorr (A)	Corrosion rate (mm/yr)	Polarization resistance (Ω)
Control	-4.07E+00	-5.69E+00	-0.346	7.05E-04	6.49E+00	3.65E+01
20%	-1.81E+00	-4.19E+00	-0.341	3.09E-04	2.84E+00	8.32E+01
40%	-2.81E+00	-3.80E+00	-0.350	3.34E-04	3.08E+00	7.69E+01
60%	-5.13E+00	-1.68E+01	-0.326	1.49E-04	1.37E+00	1.73E+02
80%	-1.76E+01	-4.57E+00	-0.346	1.67E-04	1.54E+00	1.54E+02
100% -as extr.	3.19E+00	-9.66E+00	-0.603	3.74E-06	3.44E-02	6.88E+03

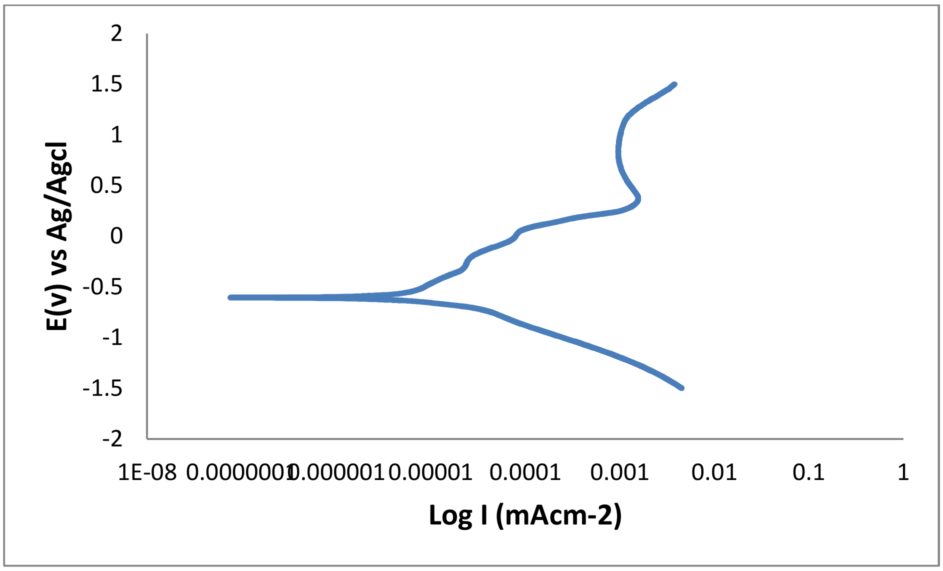


Figure 9:Polarization curve of brass in garlic extract

As indicated by the results obtained in this investigation, the overall corrosion reactions parameter profile, obviously show the alpha brass test specimens to undergo corrosion in 0.5M HNO_3 when not inhibited by any inhibitor concentration The different concentrations of the garlic extract used as inhibitor, however, clearly show progressive inhibition which improves in most cases with increase in the extract inhibitor concentration. As observed, a near perfect inhibition was achieved with the as-extracted (100%) garlic concentration. There was no corrosion loss observed and all the electrochemical data showed very passive corrosion reactions.

Summary

The composition of garlic is very complex. Garlic consists among others, of sulphur, (S), nitrogen (N), and oxygen (O). These are heteroatoms that are present in the ring structure of garlic's chemical constituents and are known [22] to have remarkable inhibitory effect which facilitates their adsorption on the metal surface following the sequence O < N < S. The inhibition efficiency of an inhibitor such as garlic extract, therefore, depends not only on the characteristic of the environment in which it acts and the nature of the metal surface. It also depends on the structure of the inhibitor itself which has been described to include the number of adsorption active centres in the molecule, the charge density, the molecular size, the mode of adsorption and the formation of metallic complexes [23].

In this research work, the results of the electrochemical tests are very much in agreement with the gravimetric tests. The effectiveness of the inhibitory properties of garlic extract in the HNO_3 test environments is confirmed. The overall results of the extract concentrations as earlier mentioned, that affected both the anodic and cathodic reactions according to the Tafel slope (ba and bc) values in Table 1 confirms the garlic extract inhibitor to be a mixed type inhibitor. The very complex structural compounds and multifarious constituents of garlic extract clearly exhibited electrochemical activity of effective corrosion inhibition particularly at the 100% concentration. A good corrosion inhibition of alpha brass was achieved with the use of garlic extract.

CONCLUSION

The obtained results in all the tests - gravimetric and electrochemical confirmed the extract of garlic as an effective inhibitor for alpha brass in nitric acid under the experimental conditions in which this investigation was performed.

The inhibition performance, in most cases, was concentration sensitive as all the result parameters in this work responded positively – either increasing or decreasing with increase in per cent concentration of the extract inhibitor. The best corrosion inhibition was achieved with the 100% (as - extracted) garlic extract concentration.

The effective corrosion inhibition performance of the garlic extract inhibitor is associated with its very complex composition of diverse chemical compounds / constituents

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