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Adsorption and Inhibition Behavior of Avicennia Marina for Zn Metal in Hydrochloric Acid Solution

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The protection of the dissolution of Zn in 1/2 M HCl by aqueous Avicennia marina extract (AME) has been examined utilized hydrogen liberation (HL), weight loss (WL), Tafel polarization (TP), electrochemical frequency modulation (EFM) and AC impedance (EIS) tests. The outcome data of studied extract is excellent except for corrosion hindrance and its mitigation efficiencies (IE%) increases with the rising of extract concentration and temperature rise. Likewise, the AME adsorbed on Zn surface obey Timken kind isotherm. Potentiodynamic polarization data revealed that the AME acts as mixed kind inhibitor. The results were correlated with scanning electron microscopic (SEM) studies. The efficiency gotten from the different tests was in best agreement.

Keywords: Corrosion inhibition, Avicennia marina extract, HCl, Zn, Hydrogen liberation, Weight loss, EIS, EFM

1. INTRODUCTION

Zinc is extensively utilized in the manufacturing, specifically for galvanizing procedure and it is engaged as a galvanizing substance for steel piping, nails, fencing, electronic properties and a lot of kind of equipment. It also utilized as, slabs, bars, and plates to defend ship hulls. Corrosion of zinc occurred in attendance of air and moisture due to its very activity [1-4]. In industry utilized of inhibitors to lower the dissolution rate of Zn in interaction with attacking environment. The utilized of organic assembled and inorganic, pharmaceuticals (drugs), plant extracts and dyes are established to corrosion control. Corrosion hindrance of Zn can achieve by the handling chromate, the wastes gotten from this handling outcome have strong influence on the environment [5-7]. Consequently, the environment eco-friendly corrosion mitigation has been close-fitting [8-11]. Most of the recent published literature revealed that the study of protection of different metals with various green inhibitors has been reported. A few examples are Carica Papaya and Camellia Sinensis Leaves [12], Red Peanut Skin [13], Punica granatum peel [14], Musa species peels [15], Henna extract [16], Delonix regia extracts [17], khillah (Ammivisnaga) seeds [18], opuntia extract [19], have been studied on various metals and alloys. However, only a limited number of literatures are available for the inhibition of corrosion by green inhibitors with Zn metal surface. Some investigators have been reported on Zn metal such as, Cnidoscolus Chayamansa [20], Achillea fragrantissima [21], Nictanthes plant extract [22], Allium Cepa (Onion) [23], Aloe vera [24], Ocimum tenuiflorum [25], henna (lawsonia) Leaves [26]. The natural products from plant origin enclose different organic composite (e.g., alkaloids, pigments, tannins amino acids) and most are recognized to have protective action [27-28]. Other authors have also displayed that the hindrance influenced by the extract solutions was because the attendance of photochemical compounds which adsorbed on the metal surface [29] and blocks the active center in surface of metal and thus prevent corrosion process. AME has been established to enclose inconsistency of natural produce components, containing flavones, naphthalene derivatives, prenylpropanoid glycosides, iridoid glucosides and abietane ditrerpenoid glucosides [30]. Conventionally, it is utilizing in Egypt against fish stings to cure skin diseases, ringworms, sores, boils, skin ulcers and scabies [31-32]. In the literature, AME has been describing to demonstrate antifertility [33-36].

In our present attention is to educate the influence of corrosion hindrance and the adsorption performance of eco-friendly environment by (AME) on Zn corrosion in 1/2 M HCl solution.

2. EXPERIMENTAL METHODS

2.1. Specimen preparation

The Zn metal coins of composition: Cd 0.04%, Pb 1.03%, Fe 0.001%, Cu 0.003% and the rest being Zn and area of 3cm x3cm x 0.08cm were utilized for WL and electrochemical tests. Zn coins were polished with unlike grades of emery papers from 320-1300, washing with acetone then dried.

2.2. Preparation of acidic chloride solution

The acid solution of 1.0 M HCl was prepared by dilution of HCl (37%) with bi-distilled water and all tests have done in unstirred solutions.

2.3. Preparation of plant extract

Avicennia marina leaves were collects from the source and dried under shadow for about 48 hours, grinded well, then soaked in a solution of bi-distilled water, sieving the hanging contaminations, and assembly 1000 ppm as a stock solution. Different concentrations were prepared using bi-distilled water and used throughout our present investigation.

2.4. Weight loss (WL) Measurements

Zn metal specimens were used for WL measurements. WL studies have approved as stated earlier [37]. From the WL experiments the % (IE) and (θ) were measured by utilizing the next equation:

$$IE\ (\%) = \Theta \times 100 = [1 - W/W^{o}] \times 100 \qquad (1)$$

Where W_o and W_i are the weight loss of Zn in the absence and presence of AME, individually. The dissolution rate (CR) was measured according to the next equation:

$$CR = W/St \qquad (2)$$

Where W is the average mass loss of specimens of Zn, S (cm^2) is the area, t (min) is the immersion period.

2.5. Electrochemical measurements

Three electrodes utilized in the electrochemical cell. The Zn disc acts as working electrode (WE) was with size 0.5 cm^2. (SCE) is saturated calomel electrode. Third is a platinum plate of surface size of 1 cm^2 as counter electrode. The WE was dipped in the test solution and to wait 30 min for (E_{ocp}) to be stable. The PP diagrams were carried out by polarization from -0.4 V to -1.5 V. All tests were obtained with Zn electrode in 1/2 M HCl in the nonexistence and existence of different concentrations (50 – 500 ppm) of the AME extract at 25^{o}C. The data from PP were measured from the next equation:

$$IE\ \% = \Theta\ x\ 100 = [1-(i_{inh}/i_{free})]\ x\ 100 \qquad (3)$$

Where i_{inh} is dissolution current in presence of inhibitor and i_{free} is dissolution current in absence of extract.

EIS measurements have attained utilizing the similar cell that utilized in PP experiments. Nyquist diagrams have given from the outcome of these tests. The charge transfer resistances (R_{ct}) are given from these bends by defining the variance in the EIS data at minimum and maximum frequencies, data of the double layer capacitance (C_{dl}) were measured from the next equation:

$$C_{dl} = 1/\,2\pi f_{max} \qquad (4)$$

Where, f_{max} is the imaginary frequency when EIS is a maximum. The data from the examined extract gotten was analyzed from the next Eq.:

$$IE\ \% = \theta\ x\ 100 = [(R_{ct} - R^{\circ}_{ct}) / R_{ct}] \times 100 \qquad (5)$$

Where R°_{ct} and R_{ct} are the data of resistances in nonexistence and existence of the AME, correspondingly

EFM is a non-destructive test as EIS that can straight and quickly get values of the liquefaction current without a prior awareness of Tafel constants. The important of the EFM is the causality factors (CF), which act as check the power of the EFM test. All electrochemical tests (PP, EIS and EFM) utilize (GaWLy PCI300/4). The software for analysis PP is EIS300, DC105and EFM140 for EMF test and Analyst Echem 5.21 was utilizing for value correct.

3. RESULTS AND DISCUSSION

3.1. Weight loss (WL) test

The Zn coupons dissolution rates in 1/2 M HCl without and with various concentrations of AME at 25 °C were determined in Table 1. The results achieved are potted in Fig. 1. As examination of Fig.1, the dissolution rates decreased with increasing the concentration of the extract. This designates that extract protects the dissolution of Zn in acid solution and the amount of dissolution protection balanced with the quantity of the extract existing. The data in Table 1 showed the measured data of IE, θ and C.R. in presence and absence extract. It is shown that the IE (%) rises with improving concentration of the AME. The dissolution protection is due to the adsorption of the main components of the phytochemicals molecules present in AME on the metal surface.

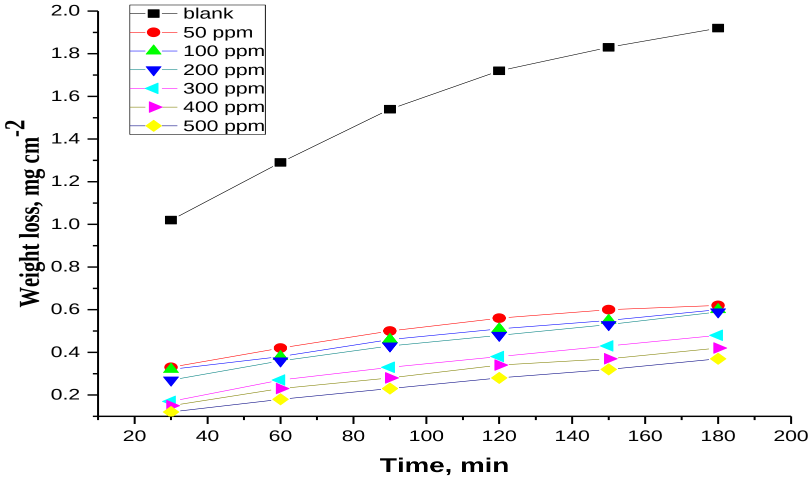


Figure 1. Wight loss-Time curves for the dissolution of Zn in absence and presence different concentrations of AME at 25°C

Table 1. Data of WL measurements for Zn metal absence and presence different concentrations of AME at 25 °C for 120 min.

Conc., Ppm	WL mg cm^{-2}	C.R., mg cm^{-2} min^{-1}	θ	IE %
0.0	1.72	0.014	---	---
50	0.56	0.0047	0.674	67.4
100	0.51	0.0042	0.703	70.3
200	0.48	0.0040	0.721	72.1
300	0.38	0.0032	0.779	77.9
400	0.34	0.0028	0.802	80.2
500	0.28	0.0023	0.837	83.7

3.2. Effect of temperature

WL method was occurring at different temperature (25–45°C) in the presence of different concentrations of AME. The corrosion rate improves with the temperature improving as shown in (Table 2). The corrosion rate of Zn metal in the absence of AME rises from 25 to 45°C whereas; in the presence of AME the corrosion rate is lowered. The rate of corrosion was lowered with rise in temperature (Table 2) and hence IE%, rises.

Table 2. Data of WL measurement for the dissolution rate (k_{corr}), θ and IE % for of Zn with different concentrations of AME after 120 minutes of immersion at 25- 45^{o}C

Temp, C^{o}	Conc., ppm	WL mg cm^{-2}	k_{corr}, mg cm^{-2} min^{-1}	θ	IE %
25	0.0	1.72	0.015	---	---
	50	0.56	0.0049	0.674	67.4
	100	0.51	0.0044	0.703	70.3
	200	0.48	0.0042	0.721	72.1
	300	0.38	0.0034	0.779	77.9
	400	0.34	0.0030	0.802	80.2
	500	0.28	0.0024	0.837	83.7
30	0.0	1.85	0.014	---	---
	50	0.59	0.0047	0.681	68.1
	100	0.53	0.0042	0.714	71.4
	200	0.48	0.0040	0.74	74.0
	300	0.39	0.0032	0.789	78.9
	400	0.33	0.0028	0.822	82.2
	500	0.29	0.0023	0.843	84.3
35	0.0	2.1	0.018	---	---
	50	0.62	0.0052	0.705	70.5
	100	0.57	0.0048	0.728	72.8
	200	0.51	0.0042	0.757	75.7
	300	0.42	0.0035	0.8	80.0
	400	0.37	0.0031	0.824	82.4
	500	0.3	0.0025	0.857	85.7
40	0.0	2.49	0.021	---	----
	50	0.72	0.0060	0.711	71.1
	100	0.63	0.0052	0.747	74.7
	200	0.56	0.0047	0.775	77.5
	300	0.43	0.0036	0.827	82.7
	400	0.37	0.0031	0.851	85.1
	500	0.32	0.0027	0.871	87.1
45	0.0	4.31	0.0359	---	---
	50	1.16	0.0097	0.731	73.1
	100	1.00	0.0083	0.768	76.8
	200	0.9	0.0075	0.791	79.1
	300	0.73	0.0061	0.831	83.1
	400	0.58	0.0048	0.865	86.5
	500	0.48	0.0040	0.889	88.9

3.3. Kinetic and thermodynamic studies

The dissolution data in the absence and presence of AME in 25–45°C has been reported in Table 3. The energy of activation (E^*_a) for Zn dissolution in 1/2 M HCl was measured from the slope of lines by utilizing Arrhenius relation:

$$Log\ k_{corr} = -E^*_a / (2.303\ RT) + log\ A \qquad (7)$$

where A is pre-exponential Arrhenius factor, R is gas constant and T is absolute temperature. By drawing 1/T vs log k_{corr} the data of E^*_a has been measured (E^*_a is (slope) 2.303 x R) Fig. 2. E^*_a for Zn reaction was improved in the presence of extract (Table 3).

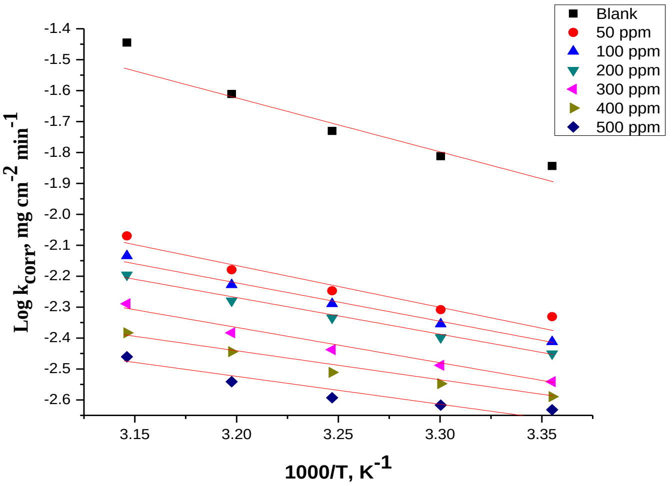


Figure 2. Log k_{corr} vs.1/ T diagrams for Zn metal in 1/2 M HCl in absence and presence of various concentrations of AME

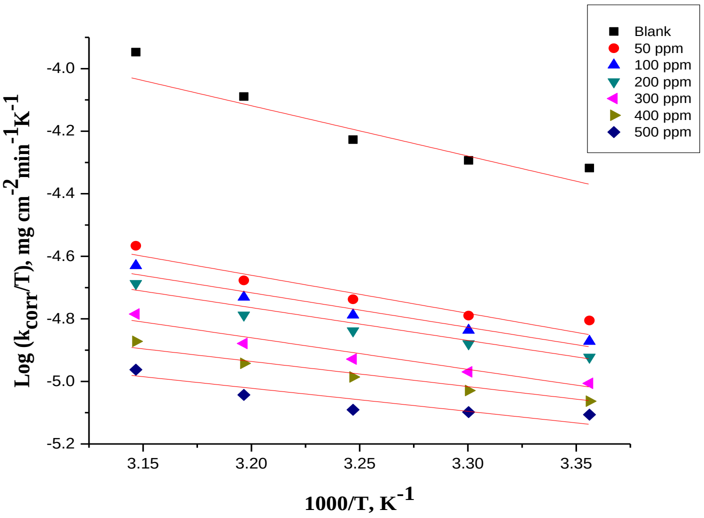


Figure 3. (Log k_{corr} / T vs 1/T diagrams) for Zn metal in 1/2 M HCl in the absence and presence of various concentrations of AME

The decrease in E_a^* with increasing of extract concentration is typical of chemisorption due to that the chemical bonds were strengthen by improving temperature, due to the formation of energy barrier on the Zn surface. This indicative to the chemical adsorption of extract components on the Zn surface as described before [38]. The data of entropy change (ΔS^*) and enthalpy change (ΔH^*) can be analyzed by utilizing the next Eq.:

$$k_{corr} = (RT/Nh) \exp (\Delta S^*/R) \exp (\Delta H^*/RT) \qquad (8)$$

where h is constant Planck's, N is Avogadro's constant, (Fig. 3) should obtain a straight lines, with an intercept is [log (R/Nh)+ΔS^*/2.303R] and a slope is (ΔH^*/2.303R) from which the data of ΔS^* and ΔH^* can be measured (Table 6). ΔH^* has positive signs which reflect the endothermic nature of the activated complex. Generally, an endothermic process indicates chemisorption. Decreasing in data of ΔS^* for the AME suggested that that activated complex in the rate-determining step signifies the association rather than dissociation step, signifying that a rise in ordering obtained on going from reactants to the activated complex [39].

Table 3. Activation data for dissolution of Zn metal in the absence and presence of different concentrations of AME in 1/2 M HCl solution

Conc., ppm	E_a^*, kJ mol^{-1}	ΔH^*, kJ mol^{-1}	$-\Delta S^*$, J mol^{-1}K^{-1}
0.0	33.4	13.4	177.8
50	25.9	10.1	212.3
100	23.7	9.2	220.2
200	22.7	8.7	224.5
300	21.9	8.4	228.8
400	18.0	6.7	242.8
500	17.3	6.1	248.5

3.4. Adsorption isotherms

The mechanism of the interaction among AME and the Zn surface can be elucidated utilizing adsorption isotherms, because, the protection of the dissolution of Zn is regularly due to either the adsorption of the AME molecules on the Zn surface or the creation of a film of insoluble metal complexes [40]. The Θ data gotten from WL were useful to plot the various adsorption isotherms (Freundlich, Frumkin, Temkin, and Langmuir). Temkin Fig. 4 was found to be the excellent, who give a graph with line straight for the plot of θ versus concentration log C [41]:

The Temkin adsorption isotherm [42] fits well the experimental data:

$$\Theta = (2.303/a) \log C + (2.303/a) \log K_{ads} \qquad (9)$$

Where C is the concentration (mol L^{-1}) of the AME and "a" is (heterogeneous factor of surface of Zn).

The relation between binding constant, K_{ads} and the standard free energy change of adsorption $\Delta G°_{ads}$ can be gotten from the next relation:

$$\log K_{ads} = - \log 55.5 - \Delta G°_{ads}/ 2.303RT \qquad (10)$$

where 55.5 is the concentration of water in solution expressed in $g^{-1}L$. ΔG^o_{ads} has negative data of designates spontaneous adsorption of the AME on Zn. Hence, the data of ΔG^o_{ads} measured were

(41.5- 47.3 kJ mol^{-1}) Table 4, ΔG^o_{ads} data up to (-20 kJ mol^{-1}) is consistent with physical process while (-40 kJmol^{-1}) describes chemical [43]. K_{ads} values decease with rise in temperature Table 4. K_{ads} values are revealing of the strength among adsorbate and adsorbent [44], their data increase with improve in temperature, this also support the chemical mechanism.

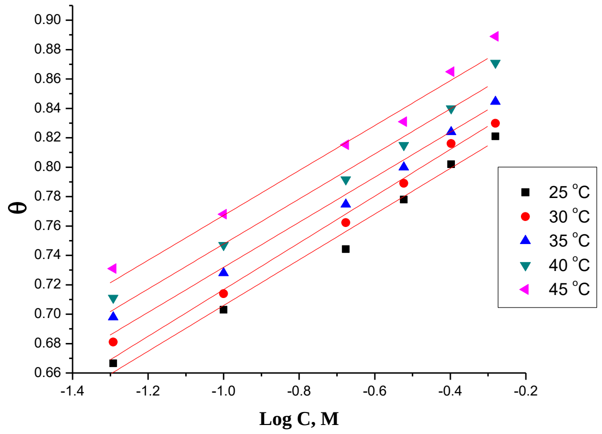


Figure 4. Temkin diagrams for of Zn dissolution containing various concentrations of AME at different temperatures

Table 4. Binding constant (K_{ads}) and standard free energy of adsorption ΔG°_{ads} for AME in 1/2 M HCl at different temperatures

Temp., K	K_{ads}, x10^{-5} M^{-1}	-ΔG°_{ads}, kJ mol^{-1}
298	3.5	41.6
303	3.2	42.1
308	6.0	44.3
313	7.6	45.1
318	10.5	47.3

3.5. Hydrogen evolution (HE) measurements

The dissolution of Zn in 1/2 M HCl with and without various concentrations of AME was occurred utilizing HE test. The relationships among the volume of H_2 evolved during the dissolution and the time is signifying in Fig. 5. The HE rate is little at the start of the reaction then improve with time. The rate of reaction is slight in the initial time interval that is called the incubation period. The rate of H_2 evolved resembles to Zn corrosion rate. Therefore, the slopes of the straight line of the diagrams were obtained as analysis of the liquefaction rates of Zn in blank and protected acid solutions. The diagram of Fig. 5 reveals that the appending of AME lower the rate of HE as the AME concentration is improved. The data of IE of different concentrations of AME are given in Table 5.

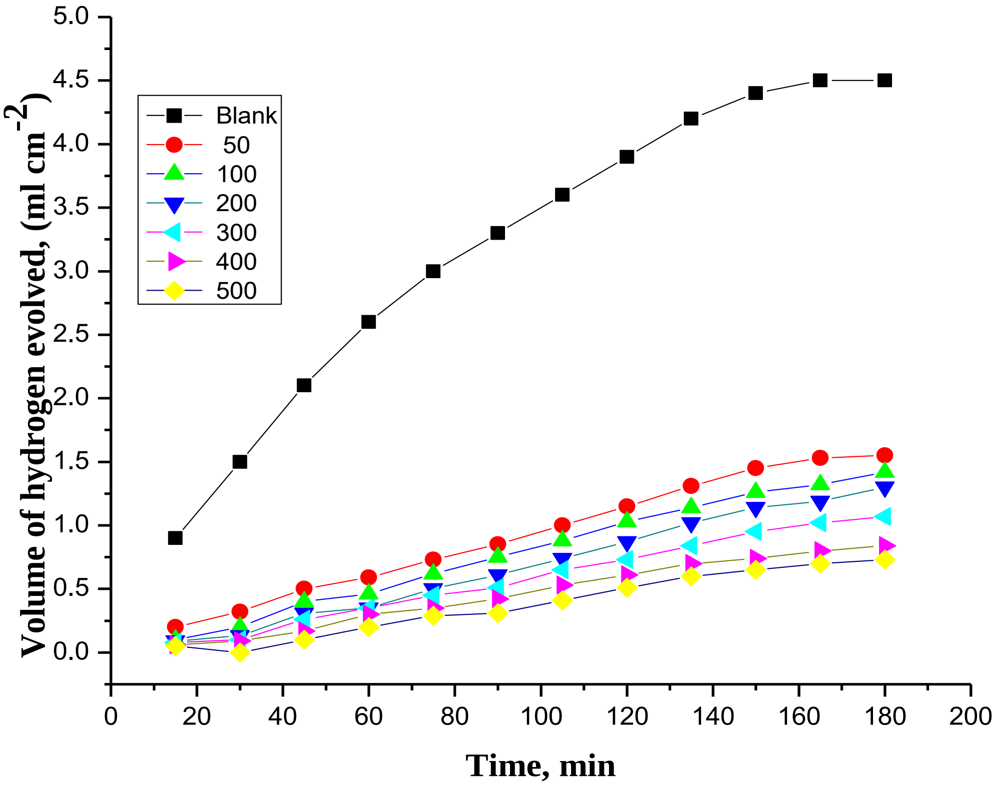


Figure 5. H_2 evolved –time curves for Zn metal corrosion in 1/2 M HCl solutions in absence and presence of different concentrations of AME at 25°C

Table 5. IE % revealed from HE measurements for Zn corrosion in absence and presence of different concentrations of AME at 25°C

Conc.(ppm)	0	50	100	200	300	400	500
IE %	----	70.5	73.6	77.7	81.3	84.3	86.9

3.6. Potentiodynamic polarization (PP) measurements

The influence of presence of numerous concentrations of AME on the cathodic and anodic polarization curves of Zn in 1/2 M HCl solution at 25°C (Fig 6) was planned. Parameters from electrochemical such as corrosion current density (i_{corr}), corrosion potential (E_{corr}), Tafel constants (β_a and β_c), and IE % were measured from Tafel diagrams shown in Table 6. It is noted from this Table that i_{corr} data decreases with the increase of the concentration of extract, due to the rise in the blocked fraction of the Zn surface by AME adsorbed. The β_a and β_c at 25ºC do not exchange unusually upon adding of AME, which designates that both anodic and cathodic measures are protected. A slight movement in E_{corr} data towards positive section was obtained in the presence of the AME representing that the mixed nature of the extract takes place.

Table 6. PP data of Zn dissolution in 1/2 M HCl and in the presence of various concentrations of AME at 25^{0}C

Conc. ppm	-$E_{corr.}$ mV vs SCE	β_a mV dec^{-1}	β_c mV dec^{-1}	i_{corr} µA cm^{-2}	IE %
Blank	1022	153	274	468	---
50	992	78	243	184	60.7
100	988	71	239	152	67.5
200	983	69	232	138	70.5
300	987	62	231	122	73.9
400	990	55	223	92	80.3
500	975	51	217	63	86.5

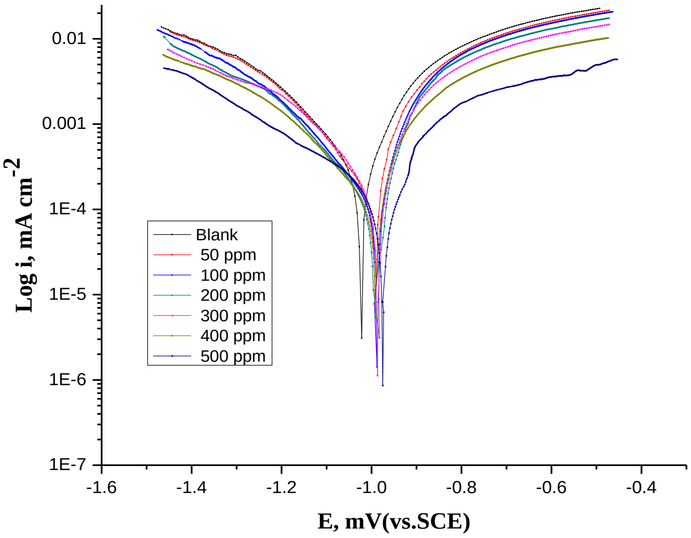


Figure 6. PP diagrams for dissolution of Zn in 1/2 M HCl in the absence and presence of various concentrations of AME at 25°C

3.7. Electrochemical impedance spectroscopy (EIS) tests

The model equivalent Randle circuit is exposed in Fig. 7 obtained for Zn in 1/2 M HCl with and without AME, where R_s (Ω cm^2) represents the solution and dissolution produces film; the parallel combination of resistor, R_{ct}, (resistance of charge transfer) and C_{dl}, (double-layer capacitance) which signifies the destroying interface

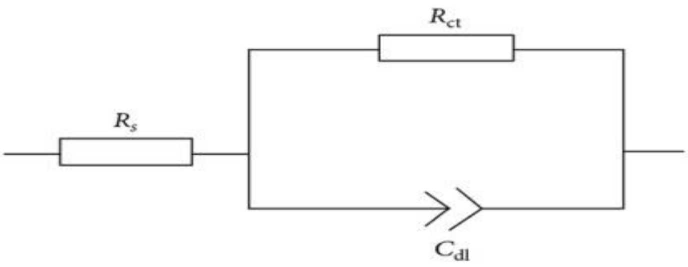


Figure 7. Equivalent circuit utilized to fit the EIS data

The Nyquist plots for Zn in 0.5 M HCl solution with and without various concentrations of AME at 25°C are showed in Fig. 8. The R_{ct} was measured from the change in EIS at upper and minor frequencies [45].

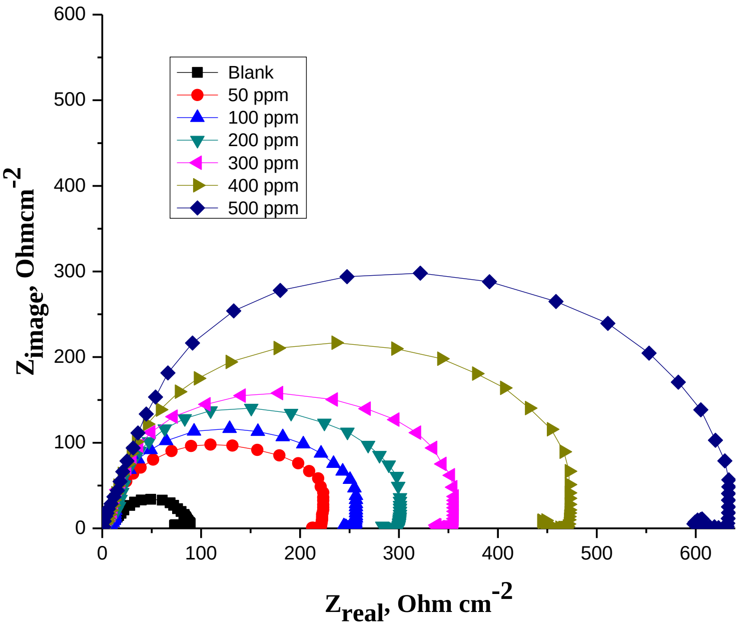


Figure 8. Nyquist diagrams of Zn electrode in 0.5 M HCl in the absence and presence of various concentrations of AME at 25ºC

From inspection of the impedance quantitative results listed in Table 7, it is seen that the R_{ct} values of the investigated extract rises with improving its concentration and this describes the formation of a protective film on the surface of Zn by the AME components adsorbed and rise in the IE in HCl. The reduction of C_{dl} data with increase of the extract concentration is due to the increase in the dielectric constant as result of replacement of the adsorbed water molecules by the inhibitor molecules and due to the increase of the thickness of the barrier film formed on the Zn surface and hence decreasing the extent of dissolution reaction [46].

Table 7. EIS parameters of Zn in 1/2 M HCl and in presence and absence of various concentrations of AME at 25°C

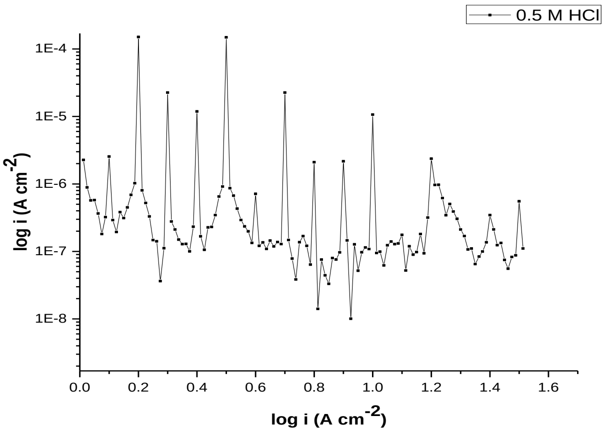
Conc., ppm	R_{ct} Ω cm^2	C_{dl} x10^{-4} F cm^{-2}	θ	IE_{EIS} %
Blank	79.79	3.031	---	---
50	223.50	2.638	0.643	64.3
100	256.56	2.3738	0.689	68.9
200	301.09	1.9389	0.735	73.5
300	356.20	1.7232	0.776	77.6
400	472.13	1.4901	0.831	83.1
500	633.25	1.2812	0.874	87.4

3.8 Electrochemical frequency modulation (EFM) tests

The EFM of Zn metal in 1/2 M HCl solution containing (50- 500 ppm) of the AME at 25°C are shown in Fig. 9. The bigger peaks were utilized to measure the i_{corr}, (β_c and β_a) and (CF-2 and CF-3) [47]. These parameters recorded in Table 8 demonstrating that this AME hinders the dissolution of Zn metal in 1/2 M HCl by adsorption. The CF obtained under various experimental test are equal to their theoretical values (2 and 3) signifying that the analyses value are verified and of excellent quality [48].

Table 7. Parameters given by EFM for Zn corrosion in the absence and presence of different concentrations of AME at 25°C

Conc. ppm	$i_{corr.}$ µA cm^{-2}	β_a , mV dec^{-1}	β_c , mV dec^{-1}	CF-2	CF-3	CR , mmy^{-1}	θ	IE%
0.0	442.1	219	453	2.00	3.46	487.7	---	---
50	165.3	91	148	1.98	3.36	182.4	0.626	62.6
100	139.3	85	136	1.97	3.97	153.6	0.685	68.5
200	96.8	77	121	1.98	3.59	106.8	0.781	78.1
300	84.4	72	111	1.95	3.55	93.2	0.809	80.9
400	68.5	68	95	1.93	3.60	75.6	0.845	84.5
500	51.7	65	78	1.96	3.7	57.1	0.883	88.3



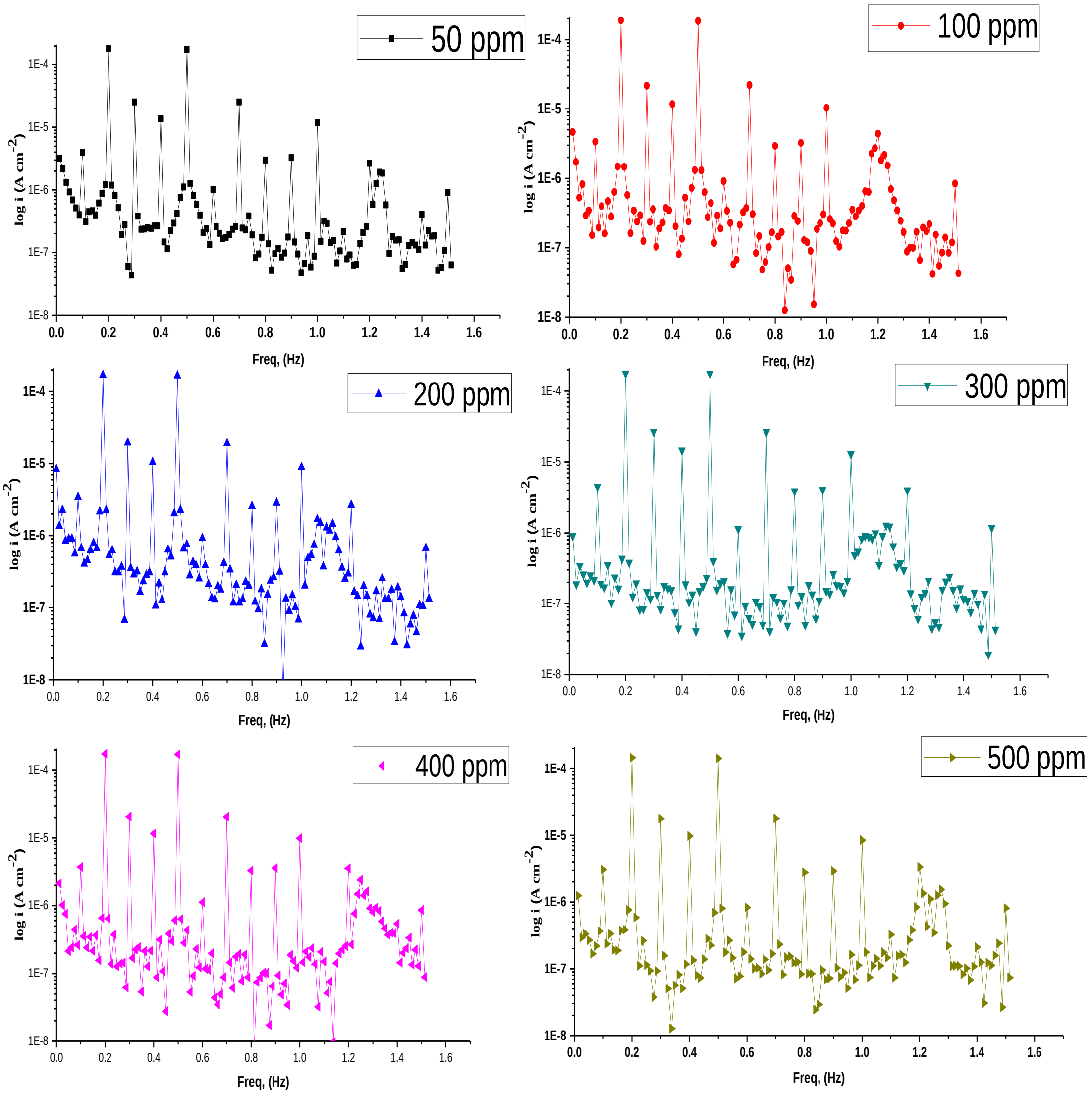


Figure 9. Intermediation spectra for Zn metal in the absence and presence of various concentrations of AME at 25 ^{o}C

3.9. Scanning electron microscopy (SEM) test

SEM microphotographs of the polished pure Zn coin was showed in Fig.10a and after immersed in 1/2 M HCl at 25 ºC for one day with and without optimum concentration of AME are depicted in Figs (10b, 10c). Fig 10b showed the Zn surface seems to be very rough in the presence of AME. Fig. 10c showed the micrographs of the Zn metal surface when unprotected to the acid medium in the existence of 500 ppm of the Avicennia marina extract, at the same magnification. In this micrograph the Zn surface was establish to be protected with smooth protective film of AME uniformly spread over the surface as previously reported [49].

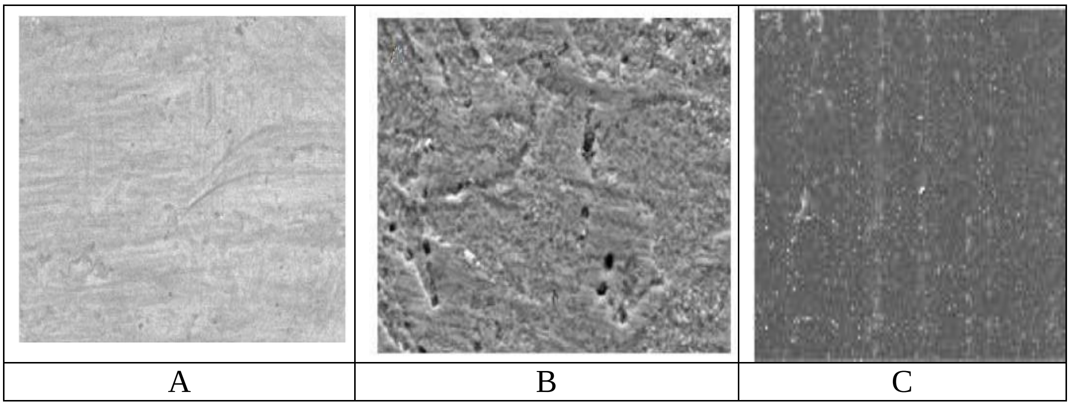


Figure 10. SEM image of Zn surface (a) before immersion in acid, (b) after 24 h of immersion in acid and (c) after 24 h of imersion in acid + AME

3.10 Explanation for inhibition

The inhibitive action of naturally occurring AME towards the dissolution of Zn metal could be qualified to the AME components adsorbed on the Zn surface that mentioned before. The basis that adsorption of the components in extract was mainly via hetero atoms existing in different components of AME in appending to the obtainability of π- electrons in the aromatic structure [50]. The above constituent's attendance in AME having many active centers at heteroatoms, which are regards as centers of adsorption. Where the outcome data of temperatures reading have shown that adsorption occurred is due to chemical adsorption. It was establish that surface of Zn in HCl has a negative sign [51] which attract the positive charged molecules (due to protonation), also many components have vacant d-orbital [52] which leads to coordination bond with the positively charge species. AME are collected of several naturally occurring organic components holding numerous N and O and O-heterocyclic rings [53]. The adsorption of these components led to decrease the reaction between Zn metal and acid media (HCl) and then decrease dissolution rate.

4. CONCLUSIONS

From the obtained results of this research, we can achieve that AME is an effective inhibitor for the dissolution of Zn in HCl 0.5 M solution at 25-45°C. The IE of AME was characteristic to the chemical adsorption of its components onto the Zn and establishes to rise with rising extract concentration and temperature. There is a best agreement among the results gotten by different tests of measurements. The AME adsorbed on a Zn surface follows Temkin isotherm. The inhibitory effect of AME results from its adsorption on the metallic surface through its electron-rich functional groups. Increase the concentration of the AME, lowers the double layer capacitances and increases the charge transfer resistance. SEM microphotographs indicate that this extract forms a protective film on the Zn due to AME adsorbed on Zn surface.

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