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INHIBITIVE ACTION AND SYNERGISTIC PERFORMANCE OF 2-AMINO-ETHANOL AND *N*,*N*-DIETHYLETHANAMINE ON COPPER IN HYDROCHLORIC ACID SOLUTION

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ABSTRACT. The corrosion inhibition action of copper alloy in 1 M HCl solution in the presence of 2-aminoethanol (A) and *N*,*N*-diethylethanamine (D) at 298 °K was investigated using gravimetric and linear polarization method. Surface studies of the copper alloy sample were observed by the help of high resolution scanning electron microscope equipped with energy dispersive spectroscopy (SEM/EDS). The evaluations were taken after 48 h interval for 288 h while the concentration of the inhibitor was varied from 5 to 10% w/v. The result of the examination shows that 2-aminoethanol (A) and *N*,*N*-diethylethanamine (D) has a good corrosion inhibition effect for copper alloy in 1 M HCl solutions and its efficiency attains above 96% at 10% w/v concentration. The linear polarization result affirmed that 2-aminoethanol (A) and *N*,*N*-diethylethanamine (D) acts as a mixed type corrosion inhibitor. Their adsorption on copper alloy has been found to obey Langmuir adsorption isotherm at all the concentration of inhibitor applied. The outcomes from all approaches are in good agreement with each other.

KEY WORDS: Electrochemical oxidation, Inhibitor**,** Synergistic assessment, Adsorption, SEM/EDX

INTRODUCTION

The engineering application of copper alloy is enormous due to their properties such as good corrosion resistance, mechanical work ability and better thermal conductivity. In electronics, it is used for making wires, sheets and tubes. While in nuclear engineering and water system they were used in condensers and cooling processes [1-8]. Atmospheric influences of copper are minimal or sometime untraceable; however, it is well-known that in aggressive media, it is vulnerable to degradation [1-2]. The dynamics of deterioration due to oxidation when in touch with liquid contaminant, solid and gas oxidizer speed up the corrosion process [9-12]. Though, copper is one of the well performed nonferrous materials with noble characteristics which make it resists many corrosive medium; however is susceptibility can be detrimental in nature. Corrosion deterioration of copper and its curtailing technique has been a major focus of recent. However, corrosion inhibitors have been seen as a notable method for restricting the occurrences. The general behavior for organic corrosion inhibitors for copper is also a concern.

In view of this, the opportunity and probability of the copper corrosion control has fascinated surface scientist on the investigation of several inhibitors in both organic and inorganic form. The chemical active molecules of some of these inhibitors like azoles [1-3], amines and amino acids [1, 11-13] among others performed better in copper. It is noticed that presence of heteroatoms such as nitrogen, sulfur, phosphorous in the organic molecule improves the action of corrosion inhibitor [9, 15-20]. 1,2,3-Benzotriazole (BTAH, $C_6H_5N_3$) has also been attested to be effective corrosion inhibitor for copper and its alloys from surface deterioration which is due to its complex active compounds or surfactant present. Mountassir and Srhiri [5] used AMT as corrosion inhibitor in sodium chloride medium with the aim of understanding the

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kinetic mechanism of copper. Deslouis *et al.* [3] studied the behavior of copper in neutral aerated solution with derivatives.

Therefore, the present study, focus on the synergistic inhibitory induced characteristics of 2-aminoethanol and *N*,*N*-diethylethanamine in acidic environment to examine the inhibitory influence on copper behavior. Dissolution mechanism process of copper has been evaluated with potentiodynamics polarization method and gravimetric technique. Corrosion rate, weight loss and inhibitory efficiency have been obtained. Surface analytical techniques using SEM/EDS was used to determine the surface photo-activity details trend of the film constituent.

EXPERIMENTAL

Sample preparation

Sectioned copper test coupons with spectrometer chemical composition in (wt %) is shown in Table 1. The dimensions were (30 x 20 x 2) mm with a 2 mm diameter hole drilled at the center top of the specimen. The coupons were polished to a mirror-like nature with emery papers and cleaned in acetone. It was further dried and weighed with an analytical balance. Each sample weight was recorded and labeled correctly. The chemicals used were of analytical reagent grade which were prepared using distilled water. Concentrations of acid were prepared by using double distilled water and the concentration range of inhibitors was 2-10% (mL), in each 40 mL of 1 M HCl. Molecular structure of the prepared inhibitor were shown in Figure 1. The electrochemical investigation was performed at 298 ^{o}K ambient temperature.

Table 1. Chemical composition of copper sample.

Element	Al	Sn	Mn	Mg	S	P	Sb	Fe	Zn	Cu
%	0.002	0.003	0.001	0.03	0.003	0.001	0.05	0.02	0.015	Balance

2-aminoethanol *N*,*N*-diethylethanamine

Figure 1. Chemical structure of 2-aminoethanol and *N*,*N*-diethylethanamine.

Gravimetric studies

At 298 ^{o}K room temperature, 40 mL of the acid solution was set up for gravimetric measurement over duration of 288 h. The weighed sample was immersed in the medium in the presence and absence of the inhibitor. The specimens were accordingly taken out in every 48 h to be washed dried and re-weighed. A gravimetric plot of weight-loss against time of immersion, corrosion rate against time and corrosion rate against concentration of inhibitor is presented in Figures 2-4.

The corrosion rate (CR) is given

$$CR = \frac{KW}{TAD} \qquad (1)$$

where K the constant is given as 87.6.

$$CR = \frac{87.6W}{DAT} \quad (2)$$

W is the weight loss in milligrams, D is the density in g/cm^2, A is the area in cm^2, T is the time of exposure in hours.

For surface area covered,

$$\Theta = \frac{W1-W2}{W1} \quad (3)$$

And the inhibitory efficiency

$$IE\% = \frac{W1-W2}{W1} X\ 100 \quad (4)$$

W_2 and W_1 are the corrosion rates in the presence and absence of inhibitor respectively.

Linear polarization resistance

Autolab PGSTAT 101 Metrohmpotentiostat/galvanostat was used to obtain linear polarization measurements for potential-current trend. The sectioned copper coupon was mounted with resin, with a surface area of 1 cm^2 and connected with electrode cell containing 40 mL of chloride electrolyte, with and without inhibitor. Graphite rod was used as auxiliary electrode and silver chloride electrode (SCE) function as reference electrode. Linear potentiodynamic potential scan range from -1.5 V to +1.5 mV at scan rate of 0.0012 V/s. The corrosion potential (*E*corr), and current density (*j*corr) data were evaluated from the Tafel plots.

The surface coverage (θ) and the percentage inhibition efficiency (*% IE*) were calculated with equation 5 and 6.

$$\Theta = 1 - \frac{Icorr}{Iocorr} \quad (5)$$

The percentage inhibition efficiency (% IE) was calculated from corrosion current density values using the equation.

$$IE\% = 1 - \frac{Icorr}{Iocorr} X\ 100 \quad (6)$$

I_{corr} is inhibited corrosion current densities and Io_{corr} is un-inhibited corrosion current density.

Morphological characterization

The structural morphology of the copper alloy samples in the absence and presence 2 aminoethanol (A) and *N*,*N*-diethylethanamine (D) was evaluated after the polarization test using VEGAS 3 TESCAN SEM/EDS. The SEM/EDS images of the metal surfaces after potentiodynamic measurement were taken.

RESULTS AND DISCUSSION

Gravimetric studies

The corrosion rate of copper alloy in the absence and presence of 2-aminoethanol (A) and *N*,*N*-diethylethanamine (D) at 298 °K was studied using the gravimetric method. Figure 2 shows the variation of weight loss of copper alloy specimen with exposure time in the absence and presence of different concentrations of A+D. This indicates that in the absence of A+D, the corrosion rate of copper alloy specimen increased to 0.0029 mm/year after 288 h of exposure time in the corrosive medium. The inhibition efficiency was found to depend on the concentration of the inhibitor. As the concentration of the inhibitor increases, the inhibition efficiency (%IE) also increases. The inhibitory action of the inhibitor against copper alloy corrosion can be ascribed to the adsorption of A+D molecules on the copper alloy surface, which restrains the dissolution of the sample by blocking the active corrosion sites and thus decreasing the corrosion rate, with increasing inhibition. The value of corrosion rate, surface coverage and inhibitor efficiency was evaluated from equation 4, 5 and 6. The concurrent graphical illustrations are shown in Figures 2 and 3.

It was evident from the results that corrosion rate decrease drastically with an increase in concentration of inhibitors. Values of weight loss also gradually increases linearly with increase in exposure time with blank sample and corrosion rate decreases rapidly with increase of exposure time in the presence of inhibitor. The influence of *N*,*N*-diethylethanamine complexes was significantly observed on gravimetric method and their corrosion inhibition efficiencies rises at 288 h with 96 IE%. Although, adsorption properties is essential when discussing the surface coverage value of inhibitive material since activity of *N*,*N*-diethylethanamine can be traced to the atom and coordinative bonds donated from the interaction of complex electrons and conjugal bonds [5].

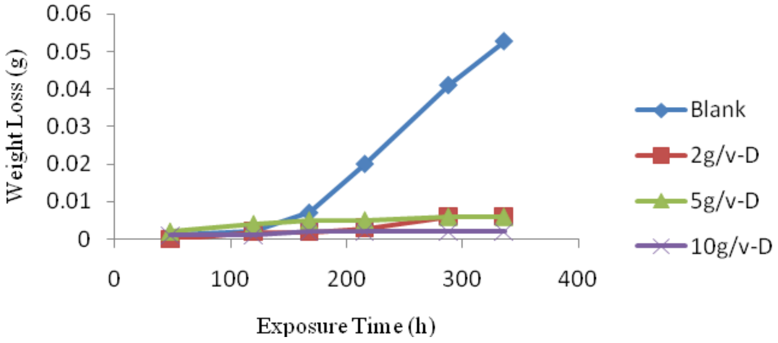

Figure 2. Variation of weight loss against time of exposure of copper in 1 M HCl solution with and without *N*,*N*-diethylethanamine.

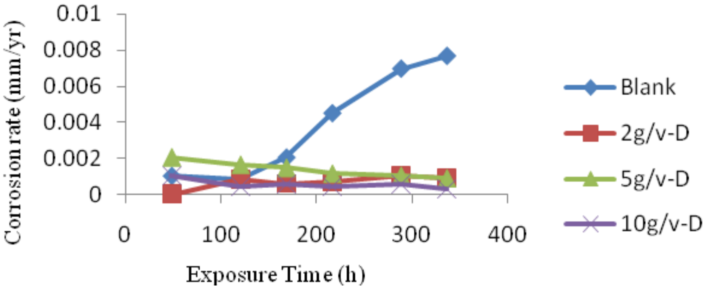

Figure 4. Variation of corrosion rate against time of exposure of copper in 1 M HCl solution with and without *N*,*N*-diethylethanamine.

Furthermore, the trend of the blank test sample increase with increasing to exposure time, indicating accelerated behaviour for the metal dissolution. This result is expected because Cl^- ion concentration has potential to enforce degradation. According to [23-25] recent report metal dissolution in HCl depend on the chloride action and the dissolution depend majorly on H^+ ion more than Cl^- infringement.

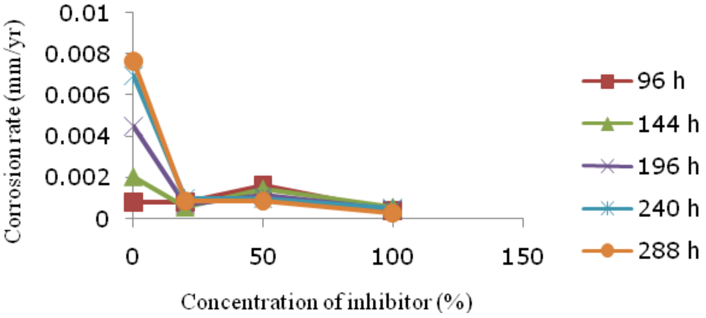

Figure 4. Variation of corrosion rate against concentration of inhibitor for copper in 1 M HCl in *N*,*N*-diethylethanamine.

At the synergistic trend in Figures 5-7, where corrosion rate, weight loss against time of exposure have a high degree of degradation with copper specimen without inhibitor. A pronounced inhibitory behavior is noticed and the rate of deterioration decrease as the concentration of the inhibitor increased. Copper behavior still maintains its stable tendency at 96 h possessing 100% inhibitory efficiency of the inhibitor. Based on these, active compounds containing heteroatoms and functional groups may be responsible for the strength acquire to retard the penetration of hydrogen ion on the copper surfaces.

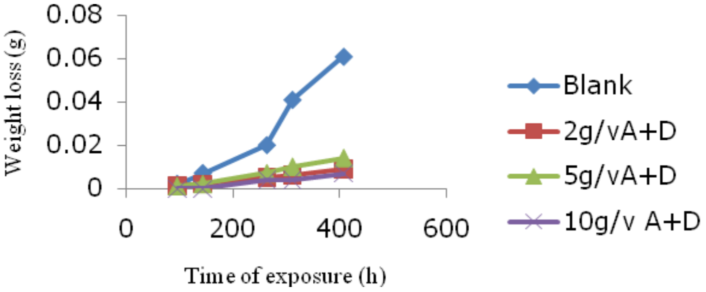

Figure 5. Synergistic variation of weight loss against time of exposure of copper in 1 M HCl solution with and without 2-aminoethanol and *N*,*N*-diethylethanamine.

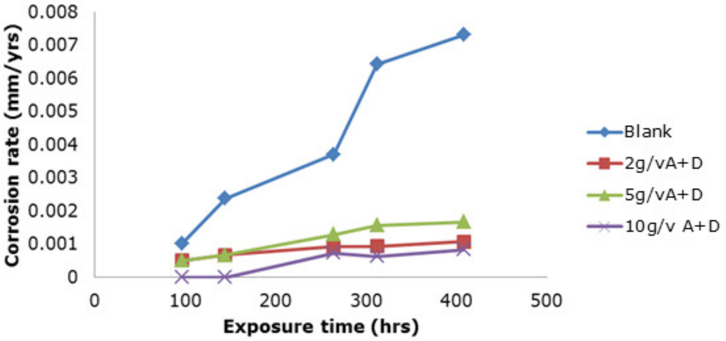

Figure 6. Synergistic variation of corrosion rate of copper against exposure time in 1 M HCl solution with and without 2-aminoethanol and *N*,*N*-diethylethanamine.

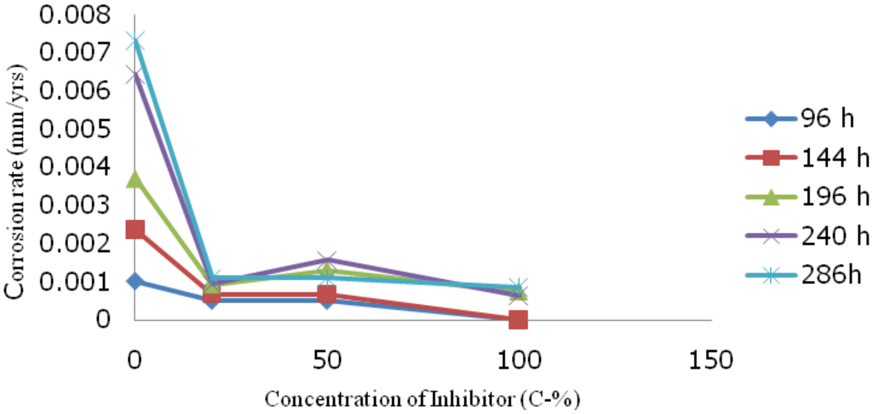

Figure 7. Synergistic variation of corrosion rate against inhibitory concentration of copper against exposure time in 1 M HCl solution with and without 2-aminoethanol and *N*,*N*-diethylethanamine.

Linear potentiodynamic polarization

Figure 8 shows the linear polarization curves of copper in 1 M hydrochloric solution at varying percentage of *N*,*N*-diethylethanamine and its synergistic characteristic with 2-aminoethanol at 298 ^{o}K. In the presence of (D) the potential appear to be less improved compared from the result obtained from the gravimetric method where *N*,*N*-diethylethanamine seem to perform efficiently at all trend compare to the as-received sample. Mean while at the synergistic behavior of [A+D] the corrosion potential shifted to the positive direction and instigated a decline in corrosion rate. This significant shift to noble regions indicates that the [A+D] helps in the blocking effect of the active site on the surface of copper sample and subsequently retard barrier for hydrogen penetration within the surfaces [3-4, 21-22].

Noticeable decreases from both the anodic and cathodic currents which cause the change in polarization movement were absolutely due to the influence of inhibitory mechanism of [A-D] even at its little concentration of inhibitor. More so, Tafel extrapolated data in Table 2 shows that the synergistic presence of [A+D] greatly decreases the deterioration rate and hence, increasing the passivity efficiency of copper. The experimental results from the potentiodynamic agree with weight-loss measurement suggesting beyond conviction the effective synergistic performance of [A+D] for copper corrosion resistance protection in 1 M HCl.

Table 2. Summary of linear polarization data obtained from copper dissolution in 1 M HCl solution with and without A+D.

Inhibitor conc.	ba (V/dec)	Bc (V/dec)	E_{corr}, (V)	j_{corr} (A/cm²)	C_R (mm/yr)	R_P (Ω)
10 mL A +D	0.023416	0.017852	-0.6147	8.74E-06	0.00701	607.79
5 mL A+D	0.55718	0.082597	-0.6245	3.68E-05	0.029537	503.60
2 mL A+D	0.015256	0.028392	-0.6554	4.67E-05	0.03763	115.19
Blank	0.55718	0.082597	-1.1121	0.000368	0.29537	84.936
2 mL D	0.028034	6.6443	-0.7556	0.000107	0.08574	113.55
5 mL D	0.77317	0.065126	-0.9233	0.000226	0.18188	92.379
10 mL D	0.016642	0.065286	-0.6425	7.43E-05	0.059682	77.495

Ba - anodic constant, Bc - cathodic constant, C_R - corrosion rate, R_p - polarization resistance.

More interestingly is the behavior of copper from increasing concentrations of [A+D] to its improved polarization resistance and significant change in the Tafel data. Ecorr value of the best inhibited copper at 10% w/v [A+D] is -0.6147 V for D ordinary is -0.7556 V compared to the as received sample with lower potential of -1.1121 V. The improved E_{corr} might be due to the mixed formation of molecule and active activity of synergistic properties of the heteroatom responsible for the inhibition which is in accordance with statement attested by [27-29]. The polarization resistance also follows the same trend with Rp value of 607.79 Ω for Cu/10 % w/v (A+D), 113.55 Ω Cu/2% w/v (D) and 84.936 Ω for as-received Cu. On the other hand, the increase in the inhibitor concentration tends to reduce drastically the corrosion rate from CR, 0.29537 of as-received sampleto 0.00701 of 10% w/v (A+D) and 0.08574 2% w/v (D) which is much expected. However, with vivid understanding of (D) performance on copper with polarization scan, one could expect that with maximum concentration better behavior or passivity should be seen at 10% w/v but this is in other way round. The behavior looked strange. However, in recent literatures it was affirmed that the potency of the inhibitors has limited inhibitory efficiency on the copper blocking interface. More so, not all inhibitor perform at high concentration of its particular environment [12-14]. Therefore, it is also important to mention at this point that the breakdown of the passive layer will also cause occurrence of pitting corrosion [28-29].

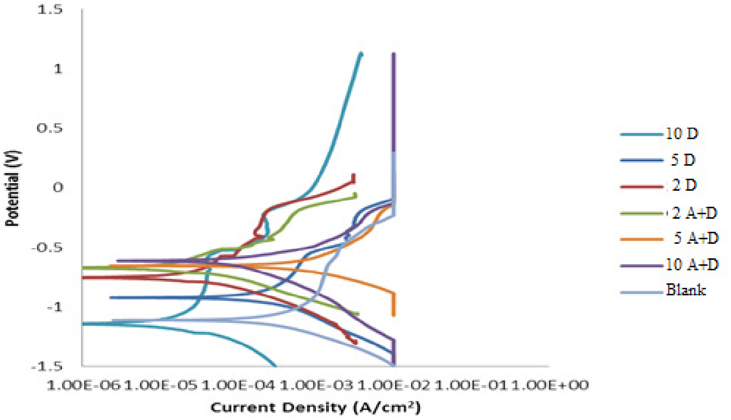

Figure 8. Synergistic linear polarization plot obtained from copper dissolution in 1 M HCl solution with and without A and D.

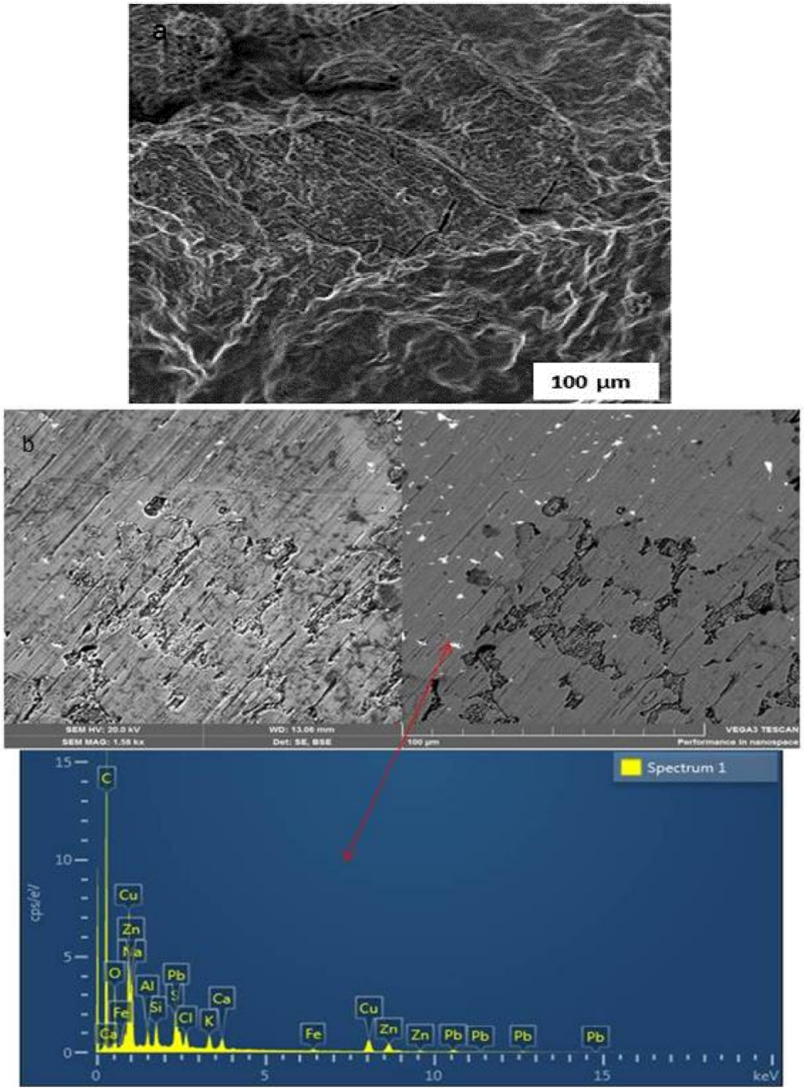

Figure 9. SE/BSE-SEM/EDX a) as-received sample and b) synergistic photomicrograph behavior of copper dissolution in 1 M HCl solution with 10% w/v concentration of [A+D].

Microstructural examination

Figure 9 shows the morphological pitting assessment of the as-received and inhibited copper sample in 1 M HCl in the presence and absence of (A+D). Breakdown and aggressive deterioration of the as-received copper sample was seen as a result of the H^+ induced penetrating at the interface. However, in the case of the inhibited sample the dissolution was not obvious except the dispatched surface corrosion product was identified through EDX elemental quantification. The possible limitation that might have change the absorbing trend of other inhibited metal resulting into slight crack or possible deterioration observed might be due to lesser inhibitory concentration and not the inhibitive effectiveness. Since dissolution of metal surface film often begins particularly at weak and expose region [3-5, 9] H^+ ion infringement must be attributed principally to the pits initiation.

More so, the substantial surface cover activities at the metal interface are mostly influenced by the chemo-physical properties of extremely molecules and heteroatom of the inhibitor [15-20]. It was also attested that they have tendency of retarding the existence of inhomogeneity in microstructure and this could basically alter the acceleration of rapid degradation of metals. Hence, the better observed photo-micrograph of the inhibited sample can be traced down to the performance and effort of the mixed inhibitor.

Mechanism of inhibition efficiency and adsorption study

Figure 10 and 11 present synergistic flow chat of inhibitory efficiency (IE) and Langmuir isotherm synergistic trend for the adsorption of (*A+D)* compounds on copper surface in 1 M HCl solution obtained in accordance with stipulated process by [22, 23]. The parameters like polarization-corrosion density (PP-Icorr), gravimetric (GM), potentiodynamic polarization-corrosion rate (PP-CR), potentiodynamic linear polarization resistance (LPR) were used to compute the plot in Figure 10. From the comparative examination, it was apparent that the inhibitory efficiency from all process agreed. This proof that adsorption of (*A+D)* compounds and its wetting potential really show maximally on copper surface in 1 M HCl solution. In this regards the phenomena of adsorption can be linked with the molecular chemical activities of the molecule, ion, and hydroxyl present.

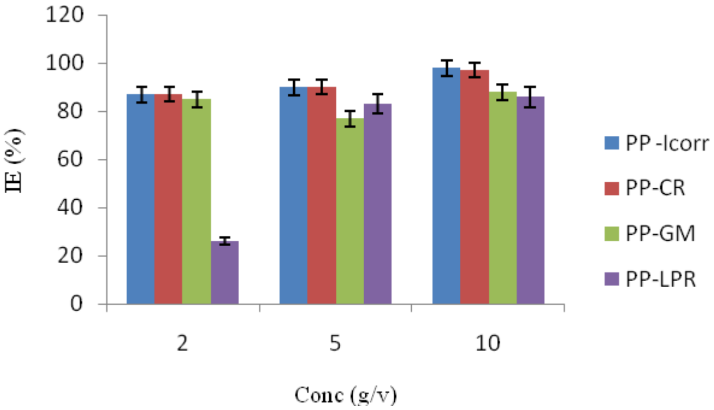

Figure 10. Synergistic inhibitory efficiency (IE) blend for 1 M HCl (*A+D*) concentration obtained from (PP-CR), (PP-I_{corr}), (PP-LPR) and (PP-GM).

In general, the adsorption characteristics of this study are centered around the molecular structure and the atom of the adsorbents inhibitor which are traced to physical adsorption between metal surface/charge atoms of the inhibitor [9-10]. The change in the current at both anodic and cathodic region acted increasingly with the concentration of the mixed inhibitor at the metal interface.

Therefore, the mechanism of these mixed inhibitory complex compounds is a blend of metal surface blockage and electrostatic force repulsion between the main adsorbed species and the medium ion. Although hydrogen evolution generated which could have produced massive impact deterioration are distorted as a result of inhibitor effort. In an attempt to understand the metal inhibitor interaction and the metallic-complex activities on the coverage site, an adsorption mechanism facilitated according [22, 26] were computed for C/θ and C for potentiodynamic polarization system using Langmuir isotherm and a linear relationship was obtained with correlation regression coefficient of $R^2 = 0.9992$ approximately (unity).

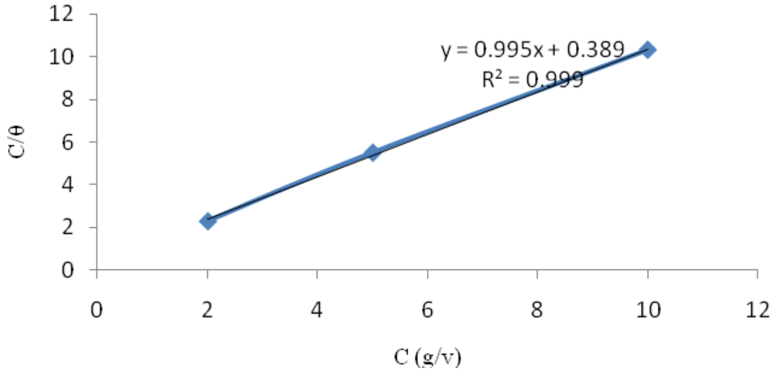

Figure 11. Langmuir isotherm synergistic trend for the adsorption of *(A+D)* compounds on copper surface in 1 M HCl solution obtained from linear potentiodynamic polarization method at 298 °K.

CONCLUSIONS

From the results obtained synergetic influence of 2-aminoethanol and *N*,*N*-diethylethanamine acts as an efficient inhibitor for copper corrosion in 1 M HCl as a result of adsorption molecules and bond structure of the inhibitor. The adsorption trend of synergetic influence of 2-aminoethanol and *N*,*N*-diethylethanamine on copper surface from 1 M HCl obeys the Langmuir adsorption isotherm. The inhibitor efficiency trends computed were determined by linear electrochemical polarization and gravimetric methods result and all agreed with each other. The surface interfacial actions of the complex molecules with mixed type inhibitory effect from polarization measurements were supported with SEM/EDS which show a good passive site for copper protection.

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