An Electrochemical and Theoretical Evaluation of Aliphatic Amino Diphosphonic Acid Derivatives Compounds as Corrosion Inhibitor for Copper in HCl Solution

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Abstract

Inhibition effect of 2AHMPDP, 10AHDDP and 3MPAHPDP on Copper alloy in 1.0M HCl solution was investigated by potentiodynamic polarization measurements in the presence of different concentrations of compound ranging from 150-450mg/l. The effects of temperature, and change of open circuit potential with immersion time were also studied. The effect of compounds on the CA Corrosion was also studied by quantum chemical calculations.

The results show that the experimental and theoretical studies agree well and confirm that 3MPAHPDP is a better inhibitor than 2AHMPDP and 10AHDDP respectively. And the results showed that aminodiphosphonic acid acts as a mixed type inhibitor in 1M HCl by suppressing simultaneously the cathodic and anodic processes. The adsorption of aminodiphosphonic acid on the CA surface obeys to the Langmuir's adsorption isotherm..

Keywords:
A. Copper
B.Electrochemical calculation
B. Quantum chemical calculations
B. Adsorption
 C. Acid corrosion

1. Introduction

  Copper and its alloys have good characteristics and a wide range of industrial applications. They have the largest number of applications as conductors of electricity and heat. Copper shows excellent performance as a structural material, because among other things, it is resistant to corrosion over a wide range of pH values. However, it is known that in aggressive media, copper is susceptible to corrosion, due to the lack of a protective passive layer in the acidic environment[1]. Copper as a structural material is often exposed to acidic conditions, e.g., during its purification, electro polishing or during the removal of corrosion products from the heat transmissions. The most commonly used acid in these processes is hydrochloric acid. The protection of copper in these processes in an acidic environment is usually accomplished with corrosion inhibitors.[2]

 Organic compounds that contain hetero-atoms such as nitrogen, sulphur and oxygen, or conjugated double bonds have shown good inhibition properties against copper corrosion[3]. This kind of organic molecules can be adsorbed at the metal-solution interface, which will reduce the corrosive attack on the metal in acidic media.[4]

  The degree of corrosion protection of these molecules depends on the strength of the interaction between the organic molecule and the metal surface atoms. The diphosphonic acid contain amine derivatives are an interesting group that act as inhibitors against the dissolution of copper in acidic electrolytes and phosphonates have a very strong interaction with surfaces[5].   The aim of this study is to investigate and interpret how the   diphosphonic acid contain amine derivatives [2-amino-1-hydroxy-2-methyl propane-1,1diyldiphosphonicacid](2AHMPDP),[10amino-1-hydroxydecan-1-diyldiphosphonicacid](10AHDDP) and [1-hydroxy-3-(methyl(pentyl) amino) propan-1,1-diyldiphosphonic acid] (3MPAHPDP) inhibits the copper corrosion in aerated 1M HCl solution and effect the alkyl group on inhibitor.

2. EXPERIMENTAL

2.1. Synthesis of aminodiphosphonic acid derivatives

Three aminodiphosphonic acid (2AHMPDP, 10AHDDP and 3MPAHPDP) with structures shown in Fig.1, were synthesized by the reaction between 2-aminoisobutyric acid, 6-aminodecanoic acid and3-(N-methyl-N-pentylamino) propanoic acid respectively with phosphorous acid (29.8g) in sulfolane (90 ml) , then the mixture solution was heated to 75^0C, for 30 minutes Afterward the mixture was cooled to 35-40^{0}C and then gradually introduced phosphoroustrichloride PCl$_3$ (83ml) while temperature maintaining at 35-45^{0}C. The mixture is heated to 63-67^{0}C for 3 hours, whereby white solid result, It is then cooled to 0-5^{0}C, and quenched by slow addition of water (250 ml) at 0-5^{0}C over a period of 1 hour. The resulting clear solution is heated at 100^{0}C for 3 hours, cooled to ambient temperature and isolated from the reaction mixture by cooling to about 0^{0}C, or by combining it with a solvent like acetone and isolated by filtration.
The structure of the compound was confirmed by FT-IR spectroscopic methods.
The IR of compound 2AHMPDP is represented in Fig. 2a
IR (KBr): 3427.37, 3143.88, 2959.71, 1603.52, 1507.58, 1192.27, 986.41cm^{-1}.

The IR of compound 10AHDDP is illustrated Fig. 2b
IR (KBr) : 3423.99, 3193.06, 2955.86, 1644.02, 1525.42, 1295.45, 1148.4, 953.145 cm^{-1}

The IR of compound 3MPAHPDP is illustrated Fig. 2c
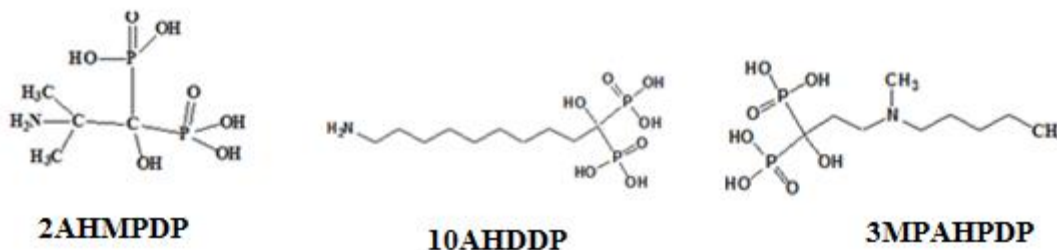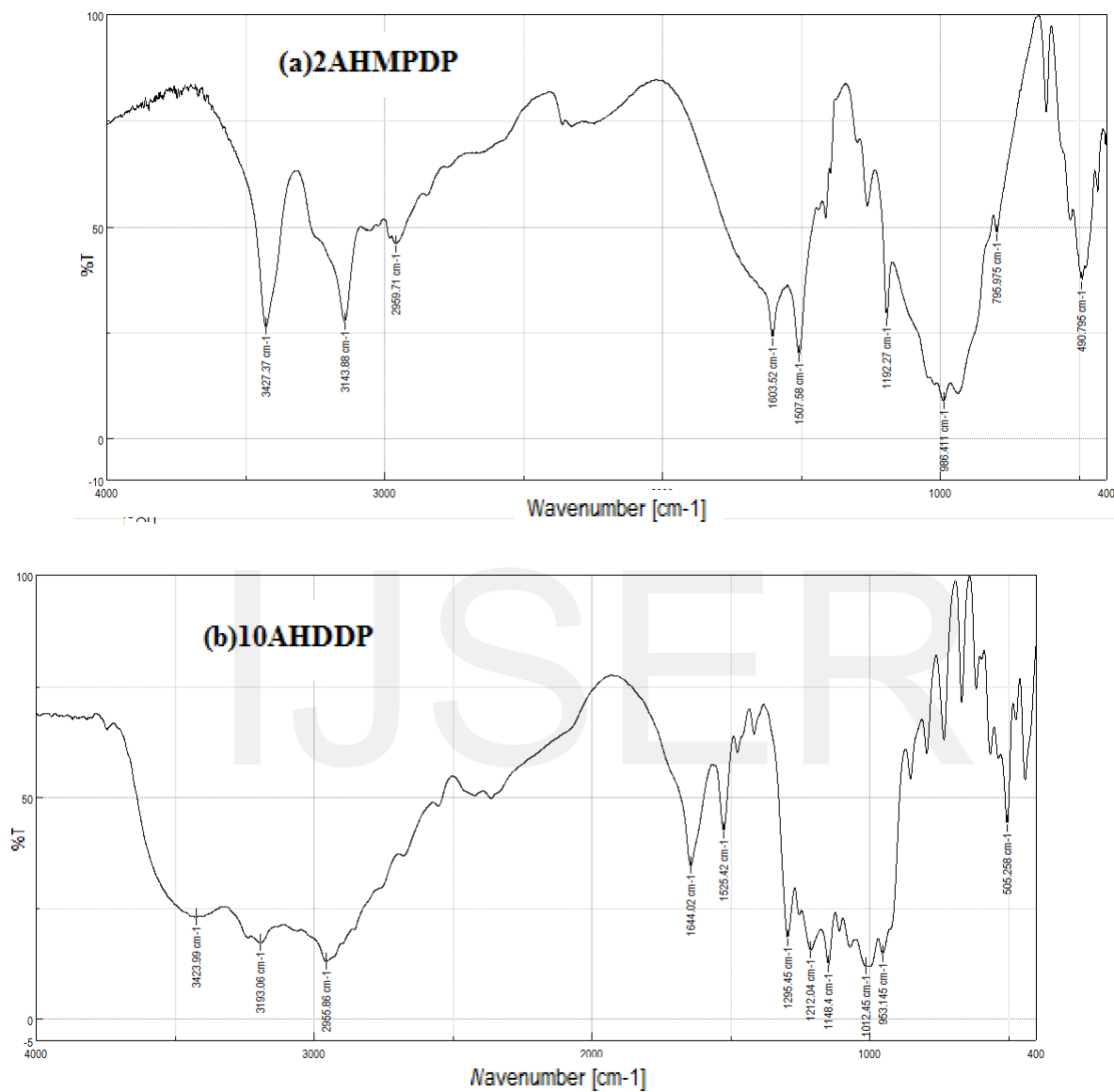IR (KBr) : 3339.62, 3207.04, 2955.38, 1666.2, 1427.55, 1161.18, 1034.62cm^{-1}

2AHMPDP   10AHDDP   3MPAHPDP

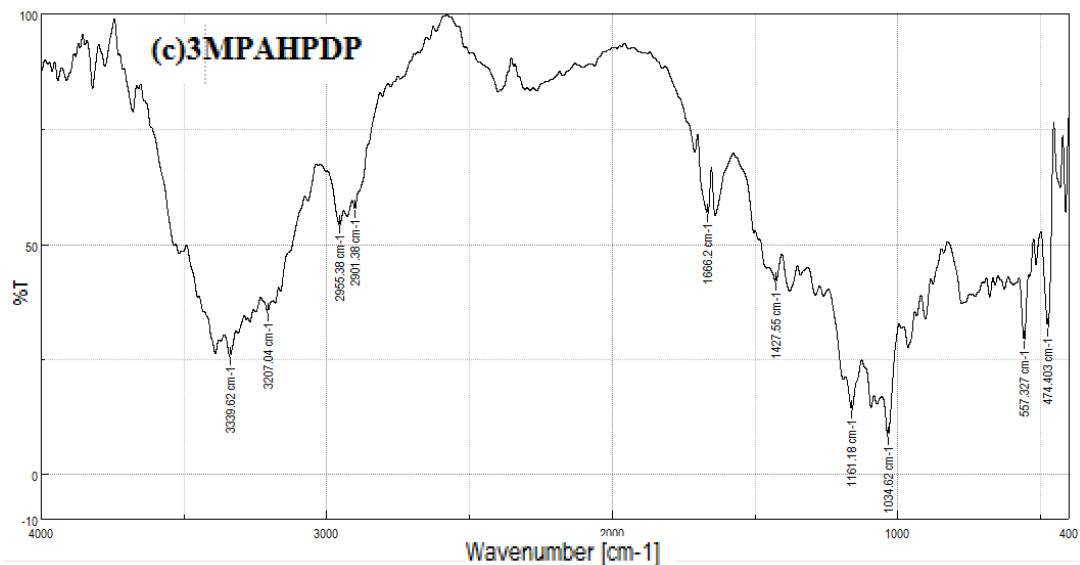**Fig. 1 Chemical structure of the synthesized inhibitors**

Fig. 2. FTIR charts of (a) 2AHMPDP , (b) 10AHDDP   and (c) 3MPAHPDP

2.2. Preparation of electrodes

The working electrode was a cylindrical disc cut from an CA rod with following chemical composition (wt.%):

Table (1) Chemical composition of the Milled steel alloys

Alloy	Composition % w/w						
	Cd	**Mn**	**Sb**	**S**	**Si**	**Ni**	**Cr**
	< 0.0030	< 0.0040	0.071	0.0077	< 0.0040	0.0094	< 0.0030
Copper alloy	**Al**	**Ag**	**Co**	**Be**	**Te**	**Zr**	**Bi**
	< 0.010	< 0.0015	0.0052	< 0.0001	0.090	< 0.0010	< 0.0080
	Fe	**Pb**	**As**	**Sn**	**Mg**	**Zn**	**Cu**
	0.092	3.08	0.024	0.0027	0.0034	38.5	58.1

The exposed surface area of 0.50 cm^2 to contact the solution. The surface pretreatment of the working electrode was carried out by grinding with different grades of emery papers down to 2000 grit. The electrode was then, rinsed with ethanol, distilled water, and finally dipped in the electrolytic cell. and finally dried in room temperature.. For each test, a freshly abraded electrode was used

2.3. Test solutions

The aggressive solutions of 1.0 M HCl were prepared by dilution of an analytical grade 37% HCl with double distilled water.

All solutions were freshly prepared from analytical grade chemical reagents using doubly distilled water. Each run was carried out in stagnant aerated 1.0 M HCl solutions without and with various concentrations (150, 250, 300, 350 and 450 mg/l) of at different immersion times (0.5 hr). The chemical structure of aminodiphosphonic acid derivatives is given in Fig. 1. For each experiment, a freshly prepared solution was used. The temperatures of the solutions during the experiments were kept at $25\pm1°C$ by controlling the cell temperature.

2.4. Electrochemical measurements

Electrochemical measurements were carried out in a conventional electrochemical cell containing three compartments for working, a platinum counter was used in the experiments due to its large surface area and high catalytic activity[6] and reference electrodes. A Luggin–Haber capillary was also included in the design. The tip of the Luggin capillary is made very close to the surface of the working electrode to minimize IR drop[7]. the Ohmic potential drop   connected to a potentiostatic (type : MLab 2 – channel : Max. current per channel $\pm100mA$; Max. CE voltage ±20 V ; current ranges 7 ; current resolution 100pA ; interfaces ; 1Rs 232 ; potential accuracy $\pm1mV$, Made in Germany . which has obtained from the BANK company , with software MLab Sci. The reference electrode was a saturated calomel electrode (SCE) used directly in contact with the working solution. The experiments were conducted in a 250 cm^3 volume cell (open to air) at $25\pm1°C$ using a temperature control water bath. All potential values were reported in V(SCE). the electrode was immersed 30 min in the electrolyte solution until a steady free corrosion potential as reached (steady state open – circuit potential Eocp)

Measuring the variation with time the open-circuit potential (Eocp) of the working electrode was also performed. This is important in defining domains of corrosion, partial and complete inhibition, and in determining inhibitor threshold concentrations[8]

2.5. Calculation methods

The molecular dynamics (MD) simulations were performed using the software, Material Studio 4.3, Discover module. Cu (2 0 0) surface was chosen for the simulation study. The MD simulation of the interaction between molecular inhibitors and the Cu (2 0 0) surface was carried out in a simulation box (19.86A - 19.86A - 38.10A) with periodic boundary conditions to model a representative part of the interface devoid of any arbitrary boundary effects. The Cu (2 0 0) plane was first cleaved from Fe crystal, and then the surface was optimized to the energy minimum. The addition of the amino diphosphonic acid molecules near to the surface was carried out and using the PCFF force field to simulate the behavior of the PCT molecules on the Cu (2 0 0) surface. The MD simulation was performed under 298 K, NVT ensemble, with a time step of 0.1 fs and simulation time of 50 ps. The interaction energy $E_{interaction}$ of the Fe surface with the PCT molecules was calculated according to the following equation:

$$E_{M\text{- inhibitor}} = E_{total} - (E_{surface} + E_{inhibitor}) \ldots\ldots\ldots (1)$$

$$E_{binding} = - E_{Cu\text{- inhibitor}}$$

where E_{total} is the total energy of Cu crystal together with the adsorbed inhibitors molecules, $E_{surface}$ and $E_{inhibiter}$ are the energy of the Cu crystal and free inhibiter molecules, respectively. And the binding energy is the negative value of the interaction energy, $E_{binding} = -E_{nteraction}$[9]

Quantum chemical calculations were conducted with DMol3 module in Materials Studio software. All electron calculations of PCT molecules were accomplished by GGA/BLYP method with a double zeta plus polarization (DNP) basis set and the choice of convergence accuracy was fine. Frequency analysis was performed to ensure the calculated structure being the minimum point on potential energy surface (without imaginary frequency).

3. Results and discussion

3.1. Experimental study

3.1.1. E_OCP vs time measurements

In the present study, the variation of the **E_OCP** of CA was followed as a function of time in aerated non-stirred 1.0 M HCl solutions in presence of three selected aminophosphonic acid at 298 K. Results obtained are showed in Fig. 3. In inhibited HCl solution the physical adsorption occurs between the positive charge of protonated inhibitor and negative charge of steel surface. So the steady state Ecorr drifts to more positive values.
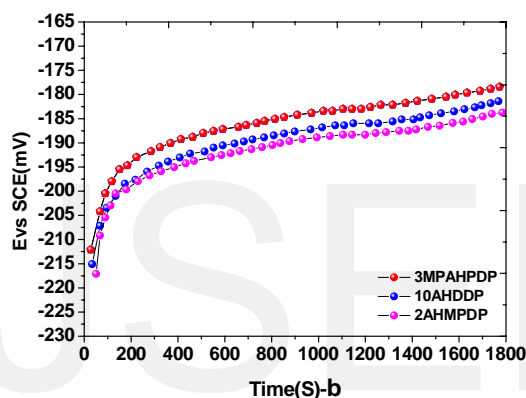

Figure 3. Open circuit potential vs time plots in CA in 1.0 M HCl

#### 3.1.2. Tafel Polarization measurements

The influence of various concentrations of inhibitors on the polarization behavior of copper alloy in 1.0 M HCl solution at 298 K was shown in Figs.4. The values of corrosion current density (icorr), Ecorr (vs.SCE), cathodic Tafel slope (ßc), anodic Tafel slope (ßa) and the inhibition efficiency (Eff.٪) deduced from the polarization curves are summarized in Table 1. The inhibition efficiencies for different inhibitor concentrations were calculated from the following equation[10] :

$$IE\% = \frac{I_{uninh.} - I_{inh.}}{I_{uninh.}} \times 100$$

where icorr(uninh) and icorr(inh) are uninhibited and inhibited corrosion current densities, respectively

As it can be clearly seen from Fig. 4 that, the addition of inhibitors to the corrosive solution both reduces anodic dissolution of CA and also retards cathodic hydrogen evolution reactions as would be expected. This may be ascribed to adsorption of the inhibitor molecules over the copper surface.

The presence of the prepared inhibitors does not remarkably shift the corrosion potential (Ecorr), while the anodic and cathodic Tafel slopes change with the increase of the alkyl group in the aminophosphonic acid. Therefore, the synthesized aminophosphonic acid can be classified as mixed type inhibitor in HCl solution [33]. The parallel cathodic Tafel lines (Fig. 5) suggested that the addition of inhibitors to the 1 M HCl solution do not modify the hydrogen evolution mechanism and the reduction of H+ ions at the copper surface which occurs mainly through a charge transfer mechanism [34]. According to values represented in Table 2, the inhibitive properties of the studied aminophosphonic acid inhibitors can be given by the following order: **3MPAHPDP >10AHDDP > 2AHMPDP** with Eff. ٪ values at 450ppm 94.04%> 94.04%> 98.98%, respectively. That is, the inhibition efficiency increased by increasing concentration. the increase Eff.٪ with **3MPAHPDP** inhibitor due to easy doner the pair electron on nitrogen and increase the adsorption on the steel surface [35]
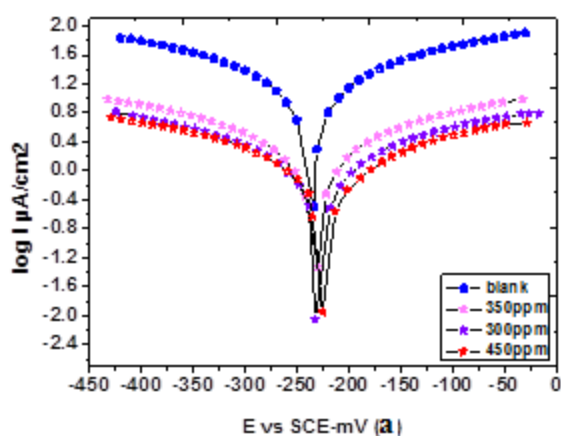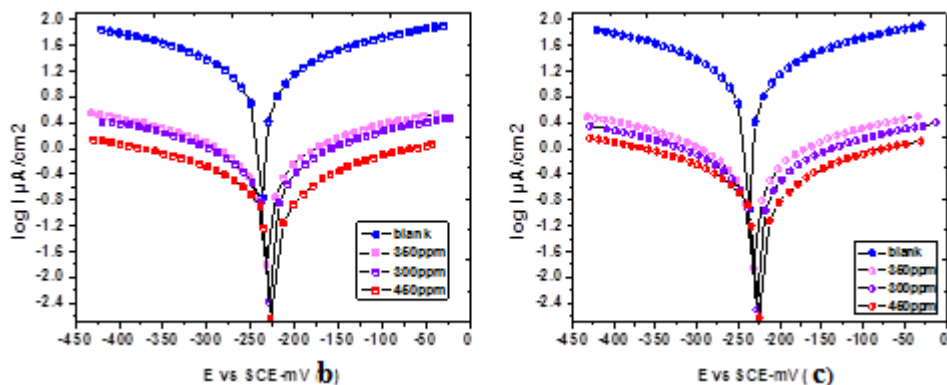
Figure 4. Polarization plots of copper alloy electrode obtained in 1.0M HCl solution and containing various concentrations of (a) 2AHMPDP , (b) 10AHDDP   and (c) 3MPAHPDP at 298 K.

Table (2): Electrochemical parameters for the corrosion of CA in the 1.0M HCl solutions with different concentration of inhibitor(a)2AHMPDP (b) 10AHDDP   (c)3MPAHPDP at 25^{0}C

a In. Conc. (mg/l)	E_{corr} (mv)	I_{corr} $\mu A/cm^2$	βa mV/ Dec	βc mV/ Dec	CR (mpy)	IE %	Ө	C/ Ө
blank	-243.9	16.78	251.3	-368.1	7.778	-	-	-
150	-243.4	2.21	229.7	-239.9	1.024	86.829	0.868	172.75
250	-240.5	1.28	-239.9	-260.1	0.593	92.371	0.923	270.64
300	-236.7	1.1	-224.3	-253.4	0.509	93.444	0.934	321.04
350	-239.9	1.41	-253.4	-257.5	0.653	91.597	0.915	382.10
450	-241.7	1	252.6	-224.3	0.463	94.040	0.940	478.51

b In. Conc. (mg/l)	E_{corr} (mv)	I_{corr} μA/cm²	βa mV/ Dec	βc mV/ Dec	CR (mpy)	IE %	Ө	C/ Ө
blank	-243.9	16.78	251.3	-368.1	7.778			
150	-234.7	1.7	143.6	-155.3	0.788	89.868	0.898	166.90
250	-242.7	1.54	157.1	-165.6	0.713	90.822	0.908	275.26
300	-238.7	1.2	132.8	-147.9	0.556	92.848	0.928	323.10
350	-239.7	1.3	257.3	-264.2	0.602	92.252	0.922	379.39
450	-244.7	0.81	199.7	-241.4	0.375	94.040	0.951	472.82

c In. Conc. (mg/l)	E_{corr} (mv)	I_{corr} μA/cm²	βa mV/ Dec	βc mV/ Dec	CR (mpy)	IE %	Ө	C/ Ө
blank	-243.9	16.78	251.3	-368.1	7.77812			
150	-244.8	0.5	222.1	-357.3	0.23176	97.02026	0.9702	154.60
250	-239.4	0.47	245.7	-345	0.21786	97.19905	0.9719	257.20
300	-232.7	0.3	254.1	-360.5	0.13906	98.21216	0.9821	305.46
350	-236.8	0.45	250.6	-354.8	0.20859	97.31824	0.9731	359.64
450	-244.2	0.17	200.9	-361.3	0.07880	98.98689	0.9898	454.60

3.2. Adsorption isotherm and standard adsorption free energy

 Basic information on the adsorption of inhibitor on metal surface can be provided by adsorption isotherm. Several isotherms including Frumkin, Langmuir, Temkin, Freundlich, Bockris–Swinkels and Flory–Huggins isotherms are employed to fit the experimental data. It is found that the adsorption of studied aminodiphosphonic acid derivatives only on carbon steel surface obeys the Langmuir adsorption isotherm equation[11] :

$$\frac{Ci}{\theta} = \frac{1}{Kad} + Ci$$

where Ci is the concentration of inhibitor, Kads the adsorptive equilibrium constant and h is the degree surface coverage **(θ = Eff./100).**

The degree of surface coverage values for various concentrations of the aminodiphosphonic acid derivatives in the1.0M HCl solution have been calculated from the average of inhibition efficiency of potentiodynamic polarization Table .2 Plots of C/θ against C yield straight lines as shown in Fig.5.

Both linear correlation coefficient (r) and slope are close to 0.998 indicating the adsorption of three aminodiphosphonic acid inhibitors on the carbon steel surface obeys Langmuir adsorption isotherm. The adsorptive equilibrium constant (K_{ads}) can be calculated from the reciprocal of the intercept of C/θ vs C curve. Generally, a large value of Kads attribute to the stronger and more stable adsorbed layer formed on the metal surface. The standard free energy of adsorption ($\Delta Gads$) can be given as the following equation[12]:

$$\Delta G^{\circ}_{ads} = -RT \, ln(55.5 \, K_{ads})$$

where R is the gas constant (8.314 J mol^{-1} K^{-1}), T the absolute temperature (K), and the value 55.5 is the concentration of water in solution expressed in molar.

The high values of K_{ads} and negative values of ΔG°_{ads} suggested that, surfactant molecules strongly adsorb on the carbon steel surface. Values of ΔG°_{ads} around -20 kJ mol^{-1} or lower are consistent with the electrostatic interaction between charged inhibitor molecules and the charged metal surface (physisorption); those around -40 kJ mol^{-1} or higher involve formation of coordinate bond between the molecules with unshared electron pairs and/or π-electrons and the metal with vacant d-orbital (chemisorptions)[13]

The obtained values of ΔG°_{ads}, -34.377,-34.779, -38.00 kJ mol^{-1} for 2AHMPDP, 10AHDDP and 3MPAHPDP, respectively. This indicates that the adsorption of inhibitors onto metal surface contain two main modes: (a) electrostatic interaction between the charged molecules and the charged metal and (b) formation of coordinate bond between the molecules with unshared electron pairs and /or π-electrons and the metal with vacant d-orbital[14,15]

The former is taken as physisorption, and the latter as chemisorption[16,17] From the structures of the inhibitors, it is apparent that the aminodiphosphonic acid derivatives exist in the forms of either neutral or cationic molecules in the acidic media. In the form of neutral molecules, the aminodiphosphonic acid derivatives can adsorb on copper alloy by the formation of coordinate bond between the molecules and Fe atoms. In the form of cationic molecules, the adsorption is predominantly related to the electrostatic interaction between the protonated

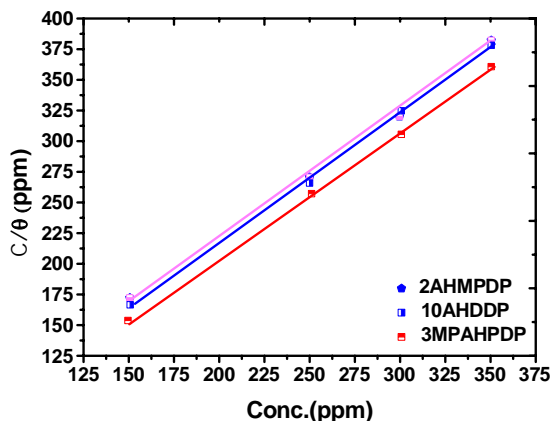compounds and copper alloy surface negatively charged by the specific adsorption of Cl_ ions [18,19] .

Figuer (5) Langmuier adsorption isotherm of the inhibition for CA in 1.0M HCl at 25^0C

Table. (3) Thermodynamic and equilibrium adsorption parameters of inhibitors on copper alloy in 1M HCl

Inhib.	1/Kad (ppm)	Kad (M‾)	$\Delta\mathring{G}$ (KJ mol^{-1})	E_a (KJ mol^{-1})
blank	-	-	-	63.37704
2AHMPDP	14.9	19000.671	-34.377	121.392
10AHDDP	11.15	22340.807	-34.779	146.667
3MPAHPDP	3.65	81947.945	-38.000	222.6813

3.3. Effect of temperature

Temperature of corrosive system affects not only corrosion rate of copper alloy in the acidic solution, but also interaction between the copper alloy surfaces and the inhibitors. In order to investigate effect of temperature, polarization measurements were applied for copper alloy in 1.0 M HCl in the absence and presence of inhibitors in the temperature range of 25–50Č . The results are shown in Fig. 6 and Table 4.

From Fig. 6 and Table 4, corrosion current density increases in both uninhibited and inhibited solutions and inhibition efficiency of the three compounds decreases

with the increase in the temperature of corrosive solutions, indicating that the three compounds are temperature-dependent inhibitors. That is to say, the increase in temperature is not in favor of the adsorption of the inhibitors on the surface of mild steel, which is indicative of the physical adsorption[20]. In addition, as seen from Table 4, the inhibition efficiency of the three compounds still follows the sequence 2AHMPDP> 10AHDDP3MPA> HPDP in the studied temperature range.

Activation energy of the corrosion process can be calculated according to the Arrhenius equation[21]:

$$\text{Ln } i_{corr} = \ln A - \frac{Ea}{RT}$$

  where A is the Arrhenius pre-exponential factor, Ea is the apparent activation energy of the corrosion process. Fig.6. depicts the Arrhenius plots of logarithm of icorr against reciprocal of temperature for copper alloy in the acidic mediums without and with of 2AHMPDP, 10AHDDP and 3MPAHPDP. According to the slopes of the lines (-Ea/R), the values of Ea are calculated and presented in Table 3. From Table 3, it can be seen that the values of Ea in the inhibited solutions are much higher than that in the uninhibited solution. Many studies state that the higher Ea for corrosion process in the presence of inhibitors than that in the absence of inhibitor is indicative of the physisorption of inhibitors[22]. However, Vracˇar and Drazˇic [23]argued that the criteria of adsorption type obtained from the change of activation energy cannot be taken as decisive due to competitive adsorption with water whose removal from the surface requires also some activation energy. On the other words, the so-called physisorption process may contain chemical process simultaneously and vice versa. Combined with the results from adsorption isotherms, therefore, we conclude that both physical and chemical processes occur in the adsorption of the compounds.

T(C°)	25			30			40			50		
Inhib.	E_{coor} (mv)	I_{corr} (µA/cm^{-2})	eff ٪	Ecoor (mv)	I_{corr} (µA/cm-2)	eff ٪	E_{coor} (m v)	I_{corr} (µA/cm-2)	eff ٪	Ecoor (v)	I_{corr} (µA/cm-2)	eff ٪
blank	-570.9	40.74	-	-578.6	48.56	-	-599.9	58.98	-	-600.1	75.75	-
2AHMPDP	-486.6	15.44	62.10	-488.8	18.9	53.60	-487.4	24.04	40.99	-493.1	33.72	17.23
10AHDDP	-483.1	14.9	63.42	-486.2	17.9	56.06	-488.2	23.36	42.66	-492.2	33.36	18.11
3MPAHPDP	-484.8	10.36	74.57	-485.2	13.12	67.79	-486.8	18.44	54.73	-490.1	26.97	33.79

Table (4)Effect of temperature on electrochemical parameters and   inhibition efficiency for copper alloy in 1.0 M HCl solution with inhibitor
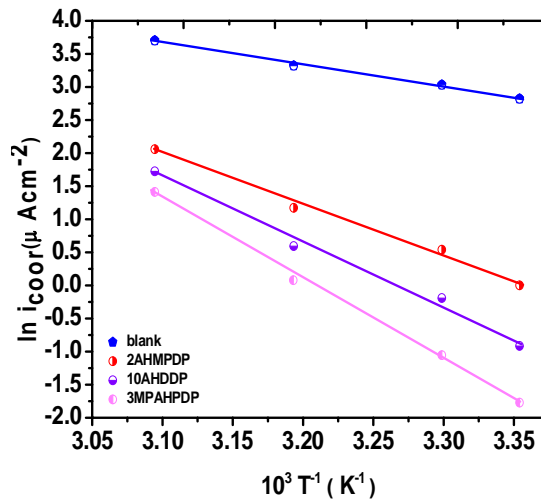

Figure (6) Arrhenius plots for copper alloy in 1.0 M HCl in the absence and presence of inhibiters.

3.4. Theoretical study
3.4.1. Quantum chemical calculations

Quantum chemical calculations were carried out to investigate the relationship between the molecular structures of the aminodiphosphonicacid derivatives and their inhibition effect. The optimized minimum energy geometrical configurations and the frontier molecule orbital density distributions of the molecules are shown in Fig. 7 In order to enrich the discussion about the electronic interaction between 2AHMPDP, 10AHDDP and 3MPAHPDP molecules with the metal surface, theoretical parameters such as molecular orbital energies (E_{HOMO}, E_{LUMO}), energy gap (ΔE),dipole moment (μ), global hardness (η) and the fraction of electrons transferred (ΔN) are useful for the understanding of their reactivities [24,25. The quantum parameters calculated for the aminophosphonic acid derivatives are shown in Table 6 The E_{HOMO} value is associated with the ability of the inhibitor molecule to donate electrons to the metal surface, therefore, higher E_{HOMO} values indicate easier donation of electrons from the corrosion inhibitor to the empty metal d orbitals. On the contrary, the value of E_{LUMO} is related to the ability of the molecule to accept electrons, lower values of this property means that the inhibitor accommodates additional negative charge from the metal surface more easily. Consequently, the ΔE (HOMO–LUMO) gap, i.e. the difference in energy between the HOMO and LUMO) is an important stability index. A lower HOMO–LUMO gap implies high stability for the molecule in the formed complex with the metal surface [26] Table 6 shows that the E_{HOMO} of 3MPAHPDP (-4.794) presents the highest value when compared with E_{HOMO} of 10AHDDP (-5.325) and 2AHMPDP (-5.784), which indicates that the structure of 3MPAHPDP may be considered the best electron donating species of the studied aminophosphonic acid derivatives. Additionally, 3MPAHPDP is characterized by having the lowest value of the energy difference (ΔE) which renders good inhibition efficiency for this species. The dipole moment (μ) provides information on the polarity of the whole molecule. High dipole moment is reflected in important molecular polarity which probably gives rise to high chemical reactivity[27]. The values of the dipole moment displayed in Tables 7 shows that: 3MPAHPDP >10AHDDP > 2AHMPDP. As for η and ΔN, they were computed based on the procedure set forth

in reference [28]. In order to calculate the fraction of electrons transferred, a theoretical value for the electronegativity(χ) of bulk iron was used χCu=4.8ev [29], and a global hardness of ηCu = 0, by assuming that for a metallic bulk the ionization potential is equal to the electron affinity [30]. From Table 7, one can observe that 3MPAHPDP has the lowest value of global hardness. The fraction of transferred electrons is also the largest for 2AHMPDP molecule. Therefore, according to a series of properties calculated for each molecule shown in Table 7, the reactivity of the aminodiphosphonic acid derivatives obeys the following order: 3MPAHPDP >10AHDDP > 2AHMPDP. As a result, a satisfactory agreement has been found between the calculated and experimental data
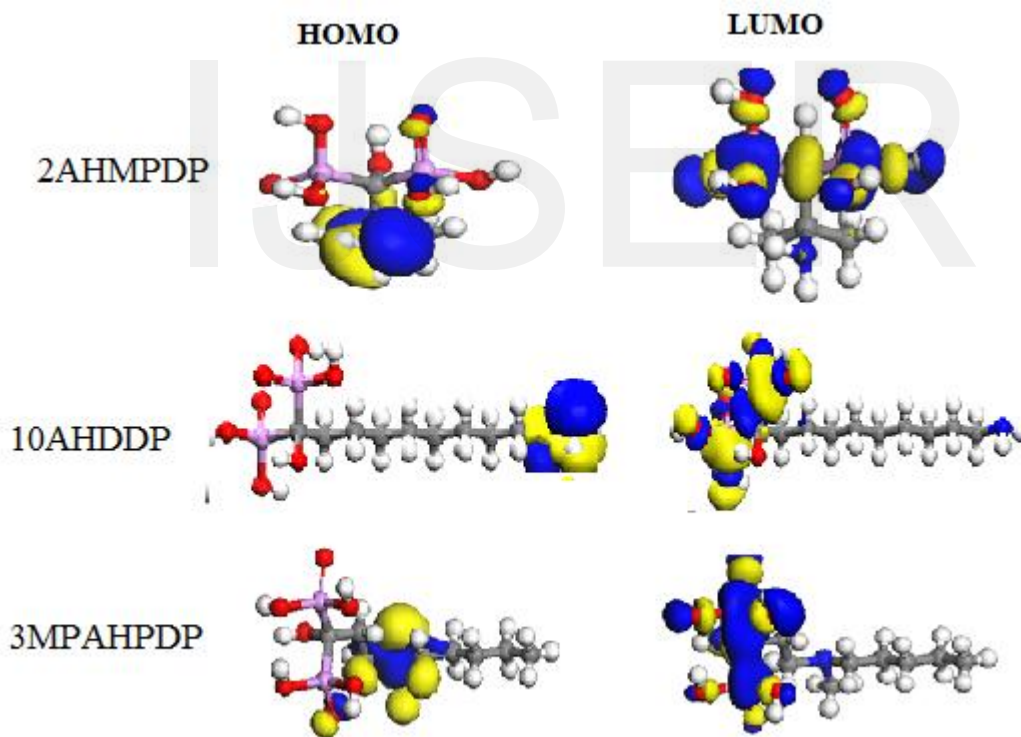
Fig(7) The HOMO and LUMO molecular orbital densities distribution of aminodiphosphonic acid derivatives

Inhibitor	E_{HOMO} (ev)	E_{LUMO} (ev)	ΔE (ev)	μ (D)	$\chi = \dfrac{(I + A)}{2}$	$\eta = \dfrac{(I - A)}{2}$	$\sigma =1/\eta$	$N= \dfrac{\chi cu - \chi inh}{2(\eta cu + \eta inh)}$
2AHMPDP	-5.784	-3.363	2.421	1.95	4.57	1.210	0.825	1.001
10AHDDP	-5.325	-3.776	1.548	4.61	4.55	0.774	1.291	1.581
3MPAHPDP	-4.794	-3.654	1.140	4.69	4.22	0.570	1.754	2.434

Table(6) The calculated quantum chemical parameters with DFT for   inhibitors in acid

3.7. Molecular dynamics simulations

The molecular dynamics simulations were performed to study the adsorption behavior of the three aminodiphosphonic acid molecules on the Cu(200) surface. The system reaches equilibrium only if both of temperature and energy reach balance. Assuming the Copper surface is clean without any ions, the values of E_{total}, $E_{surface}$ and inhibitors are obtained, and $E_{interaction}$ could be calculated according to Eq. (1).The close contacts between three aminodiphosphonic acid molecules and Copper surface as well as the best adsorption configuration for the compounds are shown in Fig.8. The calculated values of $E_{interaction}$ and $E_{binding}$ are given in Table 7. As can be seen from Fig.8, three aminodiphosphonic acid molecules are adsorbed on the Copper surface with a nearby flat orientation. As discussed in quantum chemical study, N atoms in the amino part can donate electrons to the unoccupied d-orbital of copper to form coordinate bonds, and antibonding orbital of p-electrons in diphosphonic acid part can also accept the electrons from d-orbital of copper form feedback bonds. The binding energies of the adsorption systems are 7721.22 kjmol^{-1} for 2AHMPDP, 7610.78kcal mol^{-1} 10AHDDP and 7762.68 kjmol^{-1} for 3MPAHPDP, respectively. The magnitude of binding energy is indicative of stability of adsorptive system, and higher positive value of binding energy indicates inhibitors adsorb on the iron surface easier and higher inhibition efficiency [31]. Thus a conclusion can be drawn according to the values of the binding energies in Table 7 that 3MPAHPDP adsorption system is more stable, and 3MPAHPDP exhibit the higher inhibition efficiency than 2AHMPDP and 10AHDDP . The theoretical speculation is in good agreement with the result from the electrochemical measurements.
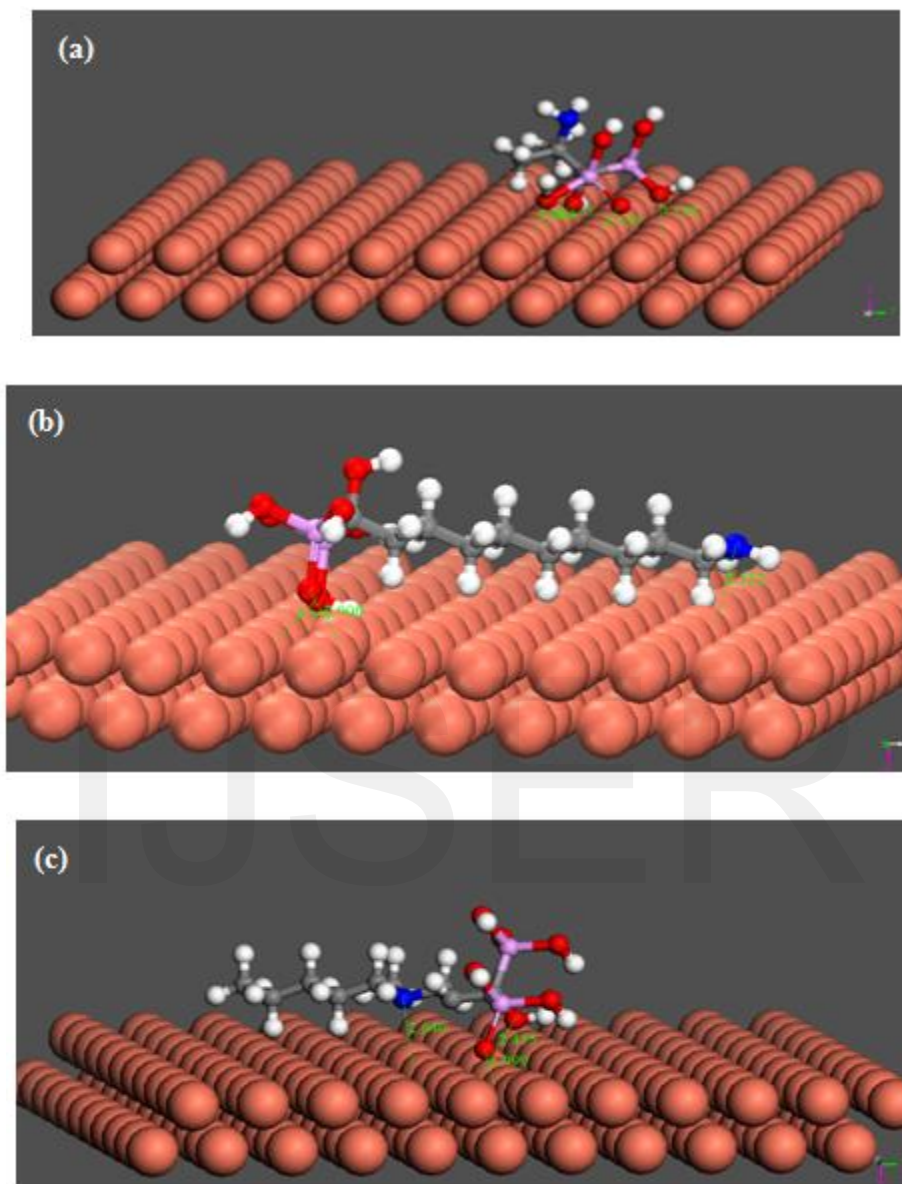
Fig. 8. Equilibrium adsorption configurations of inhibitors(a) (b)2AHMPDP(c) 10AHDDP and 3MPAHPDP on Cu (2 0 0) surface obtained by molecular dynamic simulations

Table (7) Interaction and binding energies between the aminodiphosphonic acid derivatives and Cu (2 0 0) surface.

Structure	$E_{interaction}$	$E_{binding}$
2AHMPDP	-7721.22	7721.22
10AHDDP	-7610.78	7610.78
3MPAHPDP	- 7762.68	7762.68

4. Conclusions

(1) The 2AHMPD, 10AHDDP and 3MPAHPDP show good inhibition properties for the corrosion of copper alloy in 1.0 M HCl. The inhibition efficiency increases with the increasing concentration of the inhibitors.

(2) The adsorption process of inhibitors obeys the Langmuir adsorption isotherm.

(3) Evaluation of potentiodynamic polarization measurements reveals 2AHMPD, 10AHDDP and 3MPAHPDP behave as mixed type inhibitors and suppress both anodic metal dissolution and cathodic hydrogen evolution reactions.

(4) Molecular dynamics simulation results reveal that 2AHMPD, 10AHDDP and 3MPAHPDP molecules adsorb on the copper surface.

(5) The inhibition ability of the three aminodiphosphonic acid compounds follows the order: 3MPAHPDP >10AHDDP > 2AHMPDP which has been confirmed by the electrochemical measurements and theoretical calculation measurements

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