

AB Initio Studies of Adsorption of Some Organic Inhibitors (Pyridine and Its derivatives) at the Aluminum Surface in hydrochloric acid (HCl).

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ABSTRACT

A quantum chemical study of the corrosion inhibition properties of some organic inhibitor molecules, pyridine, 2-picoline, 3-picoline, 4-picoline, 2, 4-lutidine at the aluminum surface in hydrochloric acid (HCl) was carried out. The models of the inhibitors adsorption on the Al-surface were optimized with the HF and B3LYP level using the 6-31G and LANL2DZ basis sets from the program package Gaussian 98 (A.7 Public Domain version). Based on the calculated results the compound was adsorbed on the metal surface mainly in their protonated forms. In the Al-surface is transferred to the inhibitor and organic inhibitor is adsorbed at the Al-surface in an inclined state.

INTRODUCTION

The inhibition efficiency depends on the parameters of system: metal composition, pH and structure of inhibitor molecule. It is well known that heterocyclic

Compounds containing nitrogen atoms are good corrosion inhibitors for many metals in various acidic media [1-11]. For example; benzotriazole at the Cu and Fe electrode [12-15], isoquinoline derivative [16] and imidazole derivatives [17] at the Fe electrode are sufficient inhibitors for corrosion of these metals.

Recently, it was reported that pyridine and its derivatives had been used as corrosion inhibitors of the aluminum electrode [18, 19]. Xiao-Ci, Hong, Ming-Dao, Hong-Xuan and Lu-An [20] studied the corrosion inhibition of aluminum electrode with the pyridine and its derivatives by means of a basic quantum chemical method (MNDO).

In this paper is discussed the effect of five organic inhibitors (Pyridine, 2-Picoline, 3-Picoline, 4-Picoline, 2,4-Lutidine) on the inhibition of Al-surface in acidic media by means of an advanced quantum chemical method (HF and B3LYP). The electronic structure of the organic inhibitors has a key influence on the corrosion inhibition efficiency the metal.

METHOD OF THEORETICAL CALCULATIONS

In this account calculation all calculations have been carried out using the HF and B3LYP method and the 6-31G and LANL2DZ basis sets from the program package Gaussian 98 (A.7 Public Domain Version).

THEORY AND CALCULATED VALUES OF QUANTUM CHEMISTRY

For each of crystal systems, there are in principle an infinite number of possible surfaces which can be exposed. In practice, however, only a limited number of planes are found to exist in any significant amount and we can concentrate our attention on these surfaces. Furthermore, it is possible to predict the ideal atomic arrangement at a given surface of a particular metal by considering how the bulk structure is intersected by the surface. Firstly, however, we need to look in detail at the bulk crystal structures. Aluminum, the third most abundant element in the earth's crust. The properties of aluminum vary significantly according to purity and alloying.

Aluminum crystallizes in the face-centered cubic system having a unit cell of 0.40496 nm at 20°C. The unit cell contains four atoms and has a coordination number of 12. The distance of closest approach of atoms is 0.28630 nm [21]. In this model, we use the Al-surface formed by 18 atoms on (111) crystal plane of Al (see Fig.1).

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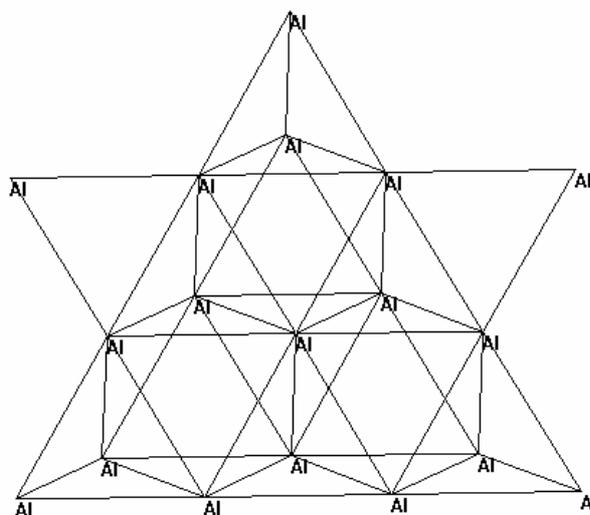


Fig.1. Two layers of Al-surface formed by 18 atoms on (111) crystal plane .

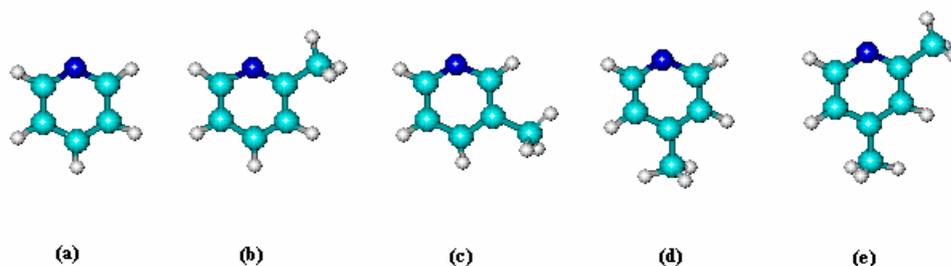


Fig. 2. (a)Pyridine [and its derivatives, (b) 2-picoline, (c) 3-picoline, (d) 4-picoline, (e) 2, 4-lutidine].

Pyridine, C_5H_5N , is a mixed heterocyclic compound containing one nitrogen atom. Pyridine and its homologues are commonly called pyridine bases. Pyridine is miscible in all proportions with water and most common organic solvents and has a boiling point $35^\circ C$ higher than benzene. Pyridine and alky pyridines are produced commercially by synthesis as well as coal tar. Commercially important compounds are pyridine, 2-methylpyridine (2-picoline), 3-methylpyridine (3-picoline), 4-methylpyridine (4-picoline), 2,4-dimethylpyridine (2,4-lutidine) (Fig.2.) [21].

Then the adsorption model of pyridine and its derivatives on the Al-surface were optimized by Gaussian. The stabilization Energy, E_s , is given as:

$$E_s = E_p - E_r \quad (1)$$

Where E_p represents the total energy of the given adsorption model consisting of protonated pyridine derivatives and the Al-surface, E_r is the sum of the total energy of the free protonated molecule of the inhibitor and the energy of the Al-surface without

interaction. Other electronic properties calculated include the net atomic charge, Q ; the change value of the net charge of the $-NH^+$ group in the pyridine ring, ΔQ_{NH^+} ; the net charge change of the Al-surface, $\Delta Q_{Al-surface}$; the adsorption distance, R ; adsorption angle, A ; adsorption dihedral angle, D .

DISCUSSION AND RESULTS

Inhibitors usually only reduce corrosion; but in some cases, like closed water systems, proper inhibition can virtually eliminate corrosion. Most inhibitors prevent or reduce of aluminum by either the anodic or the cathodic reactions. Chromates suppress the anodic reactions and chromate conversion coatings have been a widely used inhibitor for aluminum sheet. In recent years, use of chromates has decreased because of concerns for personnel and environmental toxicity. If anodic inhibitors are used in insufficient amounts, they may only restrict corrosion to fewer sites and actually increase corrosion at those localized sites.

Most other inhibitors (phosphates, silicates, nitrates, nitrites, benzoates, N-heterocyclic compounds and others), used either alone or

combination, affect the cathodic reactions. Inhibitors of this type have been used to effectively treat water systems, particularly closed systems [21]. In this paper the electronic structure of both inhibitor and aluminium surface is important. The efficiency of an organic inhibitor of metallic corrosion does not only depend on the structure of the inhibitor molecule, but also characteristics of the environment in which it acts, on the nature of the metal and the other experimental conditions. Under certain conditions of the experiment, the electronic structure of the organic inhibitors has a key influence on the corrosion inhibition efficiency to the metal.

In this model, inhibitor molecule is adsorbed at the Al-surface in an inclined state (Fig.3).we found distance between N atom in the pyridine ring and Al (1) atom in the Al-surface.Their common point is that the N atom in the ring is nearer to the Al-surface. Since the pyridine ring has three double bonds, six π -electron exist, which are sufficient for aromatic ring formation without involving the lone

pair electrons of nitrogen atom. However, the nitrogen atom has a higher electronegativity than the carbon atoms [22].

Correlation of the inhibition efficiencies with the quantum chemical values of non-protonated pyridine derivatives.

From Table.1. We find that the corrosion inhibition efficiencies might relate to the stabilization energies (E_s). The simple regressions are obtained with the inhibition efficiencies (η) and the stability energy (E_s) in the non-protonated pyridine derivatives in table 1.The linear regression shows the following relationships:

$$\eta = -25.6524 - 4.1428 E_s \quad R=-0.40279 \quad (2)$$

Where R is the correlation coefficient. It shows that the correlation is disappointing.

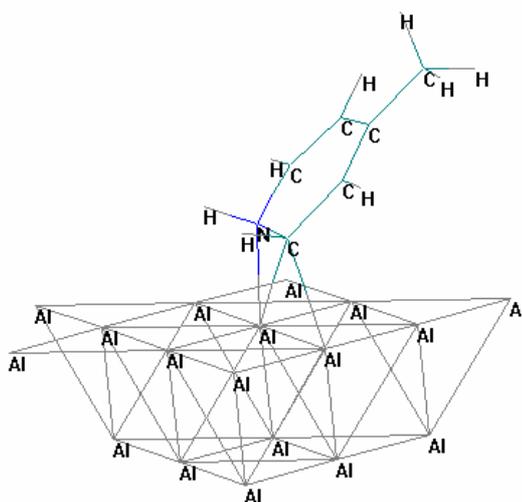


Fig.3. Adsorption protonated pyridine derivative at the Al-surface in acidic media.

Table.1.The quantum mechanical calculated of non-protonated pyridine and its derivatives.

Inhibitor	$R_{N-Al(1)} (A^\circ)$	$A_{C(20)-N(19)-Al(1)}$	$D_{C(20)-N(19)-Al(1)-Al(4)}$	$E_s (\text{kcal/mol})$	$\Delta Q_N (e)$	$\Delta Q_{Al\text{-surface}} (e)$	η
Pyridine	1.7774	88.8968	-11.8967	-19.9390	-0.3625	0.5693	20.8
2-Picoline	1.7945	146.5161	-32.2029	-25.3315	-0.3799	0.5379	65.65
3-Picoline	1.7790	142.8958	84.9337	-18.9140	-0.3711	0.5551	60.0
4-Picoline	1.7707	144.2381	15.1716	-19.4804	-0.3713	0.6184	67.43
2,4-Lutidine	1.7896	149.0195	91.5205	-22.8180	-0.3783	0.5609	99

η is the inhibition efficiency of pyridine and its derivatives [20].

Correlation of the inhibition efficiencies with the quantum chemical values of protonated pyridine derivatives.

Pyridine and its derivatives are easily protonated in hydrochloric acid (HCl) because they are weak bases. According to the values in Table 2 and η (Table 1, the same as the following), the simple regression are obtained as follows:

$$\eta = 212.0859 + 79.7811 E_s^+ \quad R=0.9835 \quad (3)$$

Comparing Eq. (2) with Eq. (3) we can conclude that pyridine derivatives are adsorbed on the Al-surface mainly in their protonated forms.

Because the $-NH^+$ group of the protonated pyridine ring has a positive charge, it accepts the electron of the Al atoms easily, that is, it is an electron acceptor. The charge of the Al-surface is affected and turns positive by the adsorption, so the electronic transfer may be from the Al atom to the organic inhibitor through the frontier orbital of the

interface when the inhibitor is adsorbed on the Al-surface.

The N-Al adsorption distance has obtained from the optimization calculations (Table 2).

These results show that the N-Al covalent bond between the inhibitor and the Al-surface has been formed.

Table.2.The quantum mechanical calculated of adsorption models.

Inhibitor	$R_{N-Al(1)}$ (Å°)	$A_{C(20)-N(19)-Al(1)}$	$D_{C(20)-N(19)-Al(1)-Al(4)}$	E_s^+ (kcal/mol)	ΔQ_{NH^+} (e)	$\Delta Q_{Al-surface}$ (e)
Pyridine	1.9104	86.7495	-10.9617	-53.5996	-0.319476	1.11540
2-Picoline	1.9477	132.5616	-54.3351	-43.3140	-0.313265	1.079298
3-Picoline	1.9212	127.136	59.6346	-45.5239	-0.319269	1.091787
4-Picoline	1.9186	126.513	-7.8007	-42.8497	-0.305127	1.090393
2,4-Lutidine	1.9606	134.3384	63.1696	-31.5758	-0.304904	1.041168

$E_s^+ = E_p - E_r$, here E_p represents the total energy of the given adsorption model consisted of protonated pyridine derivatives and the Al-surface, E_r is the sum of the total energy of the free protonated molecule of the inhibitor and the total energy of the Al-surface without interaction.

ΔQ_{NH^+} represents the change value of the net charge of the $-NH^+$ group in the pyridine ring.

$\Delta Q_{NH^+} = Q'_{NH^+} - Q_{NH^+}$, Q'_{NH^+} is the charge of the $-NH^+$ group when the inhibitor is adsorbed on the Al-surface, $Q_{NH^+} (= Q_N + Q_H^+)$ is the net charge of the $-NH^+$ group of the protonated pyridine and its derivatives.

Co-adsorption modeling with hydrogen atom and Cl^- anion in acidic media.

The key factor of their inhibition properties is the characteristics of their electronic and molecular structure but not their molecular areas. The results optimized by the HF method show that they can be adsorbed on the Al-surface in the inclined states and the inclined angles of the inhibitors adsorbed on the Al-surface are different from each other. Their common point is the N atom in the pyridine ring is nearer to the Al-surface.

To investigate the relationship between the inhibitor adsorption and its influence on the hydrogen entry into the Al-surface, the co-adsorption of protonated pyridine with adsorbed hydrogen and Cl^- was modeled. The Al-surface with one hydrogen and one Cl^- was used as the substrate for modeling the co-adsorption (Fig.4). The results of the optimized calculation are shown in Table 3.

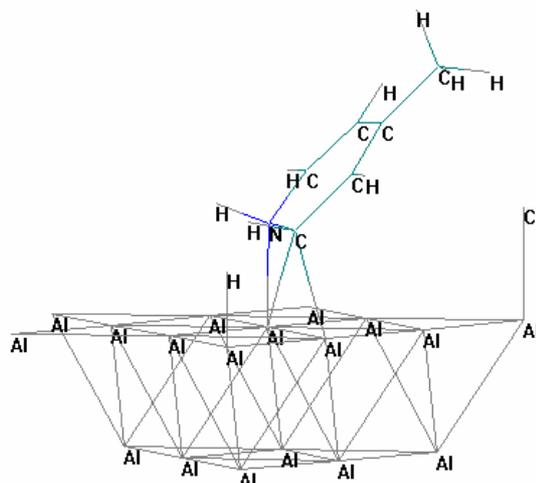


Fig.4. The co-adsorption of protonated pyridine derivative with H_{ads} and Cl^- .

Table.3.The quantum mechanical calculated of co-adsorption model with one hydrogen atom and Cl^- anion.

Inhibitor	$R_{N-Al(1)}$ (Å°)	$A_{C(20)-N(19)-Al(1)}$	$D_{C(20)-N(19)-Al(1)-Al(4)}$	$R_{H-Al(8)}$ (Å°)	$R_{Cl-Al(9)}$ (Å°)	E_s (kcal/mol)
Pyridine	1.9039	88.226	-8.2088	1.4234	2.0914	-385.2506
2-Picoline	1.9411	134.2746	-43.3963	1.4148	2.094	-374.5124
3-Picoline	1.9067	128.1313	47.5393	1.4232	2.0847	-371.8435
4-Picoline	1.9107	127.7998	1.4097	1.4219	2.0916	-371.7809
2,4-Lutidine	1.9557	137.2764	43.7559	1.4233	2.0827	-355.5989

$$E_s = E_{Al-surface+H+Cl^-+inhibitor} - (E_{Al-surface} + E_H + E_{Cl^-} + E_{inhibitor})$$

Comparing Table 3 to 2, we can find the stabilization energy increases. It may be the adsorption of Cl^- that causes the increasing of the negative charge on the Al-surface, which improves the interaction between protonated pyridine and the Al-surface. We can conclude that the adsorption of the inhibitor is possible only at a surface partially covered with hydrogen and Cl^- . It is now clear why pyridine and its derivatives can act as an inhibitor of the corrosion of aluminum.

CONCLUSION:

The following calculations are obtained:

1. The inhibition properties of the protonated pyridine and derivatives molecules are

related to the sum of the net charge and the π charge of the six-ring, respectively.

2. Pyridine and its derivatives are adsorbed on the surface of the Al electrode mainly in their protonated forms.
3. The most probable adsorption model of the inhibitors is one in which the N atom of the pyridine ring is close to the aluminum atom of the Al-surface in an inclined state.
4. AB 6-31G and LANL2DZ basis sets from the program package Gaussian 98 increases, and that of the hydrogen and Cl^- with aluminum atoms also increases.

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