

Molecular structure of imidazoline inhibitor and quantum chemical analysis of corrosion inhibition performance of Zn atom

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Abstract: The adsorption potential energy curves of imidazoline compounds and Zn atom were calculated by quantum chemistry method. The adsorption energy, imidazoline ring, the coordination bond length between nitrogen atom and Zn atom, the double atom interaction energy and the overlapping population number were obtained. The results show that the introduction of power-providing groups or substituted aromatics into imidazoline ring can enhance the chemical adsorption force between N and Zn. The calculation results can provide a useful theoretical basis for the design of corrosion inhibitors with better performance.

1 Introduction

Imidazoline type corrosion inhibitor is a kind of adsorption type corrosion inhibitor with good anticorrosion effect. There are many imidazoline derivatives because of different raw materials and different substituents on imidazoline ring. There are many reports on the experimental studies of these compounds. [1-6] Relatively speaking, there are few reports about the theoretical research, but there is no report about the relationship between molecular structure and corrosion inhibition performance by quantum chemistry method. The chemical adsorption energy of imidazoline series, series compounds and Zn atom has been calculated by quantum chemistry method, and the relationship between the adsorption energy and the corrosion inhibition property has been discussed.

2 Computational models and methods

According to the theory of chemisorption, the corrosion inhibitor molecules adsorbed chemically with the metal and formed a dense oil film on the surface of the metal. (Fig.1) Macroscopically, the oil film is composed of a single inhibitor molecule arranged on the metal surface. From the microscopic molecular level and electronic structure, the process of chemical adsorption

between single molecule and metal surface is essentially the interaction between lone pair electrons of nitrogen atom in molecule and d-orbital of Zn atom to form coordination bond. Therefore, the chemical adsorption energy and the strength of the coordination bond can be calculated by the quantum chemistry method, and the corrosion inhibition performance can be predicted. Therefore, imidazoline compounds I, II, III, IV, V and VI were calculated and studied. Fig. 2 shows the adsorption model of imidazoline compounds with Zn. The structure of compound I is shown in Fig. 3. In the structure of imidazoline compounds shown in figures 2 and 3, R₄ is the CH₂CH₂CH₃ group. Compounds II, III, IV, V and VI are represented when the R in the structure of imidazolium and morpholine compounds in Fig. 2 are H, CH(CH₃)₃, CH=CH₂, Ph-R₄ and Ph-NO₂ groups, respectively.

In this paper, the complete optimization of the above compounds is calculated by B3LYP method, Zn atom is added to the optimized equilibrium geometry, and Zn atom is connected to N atom of imidazoline ring, the distance between N and Zn atom R_{N Zn} is defined as the chemical adsorption reaction coordinate, I. E. Model II. The CNDO / 2M method is used to decrease R_{N Zn} in order to simulate and calculate the potential energy curve of chemical adsorption.

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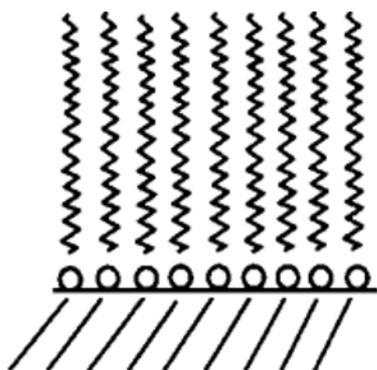


Fig. 1 Model of chemical adsorption

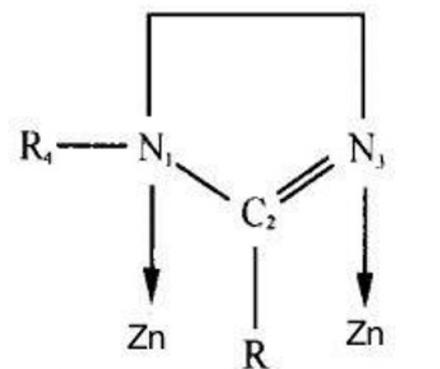


Fig. 2 Adsorption model of imidazoline and Zn atom

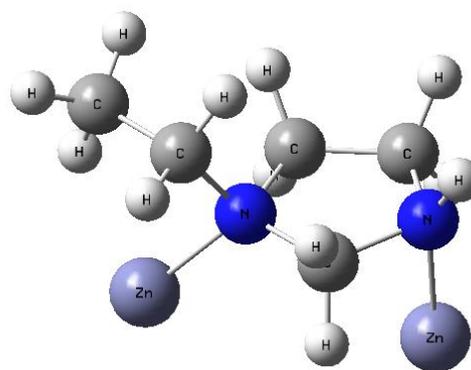
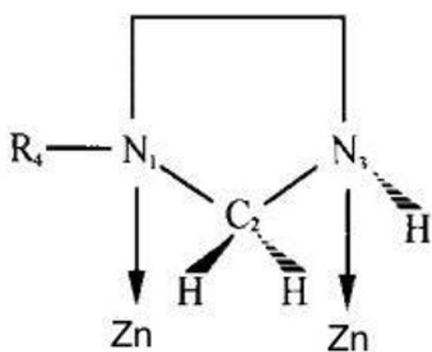


Fig. 3 Structure of compound I The results

The equilibrium geometry, net charge (QA) distribution and frontier molecular orbital(HOMO) coefficient of these compounds have been obtained by full optimization calculations using the B3LYP method. Some results are shown in Table 1. The chemical adsorption and adsorption potential energy curves of compounds I ~ VI and Zn were obtained by point-by-point optimization calculation of CNDO /

2M.(Fig.4) The adsorption energy(EADS) is obtained from the energy difference between the final state and the initial state.The distance between the adsorbed terminal state N and the Zn atom, the coordination bond length, the diatomic interaction energy(E_{N-Zn}) and the overlapping population (Q_{N-Zn}), are calculated and listed in Table 2.

Table 1 Net charge and the coefficient of HOMO contributed by N1 and N3 atoms

Compound	Coefficient of N ₁ atom			Coefficient of N ₃ atom			Q _N (Net Charge)/e	
	P _x	P _y	P _z	P _x	P _y	P _z	Q _{N1}	Q _{N3}
I	-0.1130	0.2141	0.6744	0.0488	-0.0057	0.2333	-0.4555	-0.3266
II	-0.0506	0.0956	0.6476	0.1174	-0.0989	-0.5068	-0.4547	-0.3143
III	-0.0542	0.0953	0.6403	0.1352	-0.0989	-0.5097	-0.4439	-0.3096
IV	-0.0401	0.0719	0.6378	0.1098	-0.0812	-0.5261	-0.4461	-0.3072
V	0.0613	-0.1087	-0.6388	-0.1415	0.1109	0.5042	-0.4319	-0.2988
VI	-0.0566	0.1054	0.6391	0.1214	-0.1062	-0.4949	-0.4370	-0.2918

Table 2 Chemical Adsorption f or compoundsI ~ VI and Zn atom

Compound	R _{NZn} (TS)/nm	R _{NZn} (FS)/nm	E _{NZn} (FS)/au		Q _{NZn} (FS)/e		Eabs/au
			N ₁ -Zn	N ₃ -Zn	N ₁ -Zn	N ₃ -Zn	

I	0.420	0.204	-0.4605	-0.3394	0.3751	0.3102	-0.2332
II	0.375	0.182	-0.5049	-0.5661	0.5201	0.5616	-0.3203
III	0.350	0.180	-0.5239	-0.5917	0.5307	0.5917	-0.3687
IV	0.418	0.182	-0.4685	-0.6201	0.5011	0.5810	-0.5057
V	0.330	0.180	-0.5491	-0.7074	0.5424	0.6226	-0.5644
VI	0.360	0.180	-0.4767	-0.5405	0.5105	0.5396	-0.1317

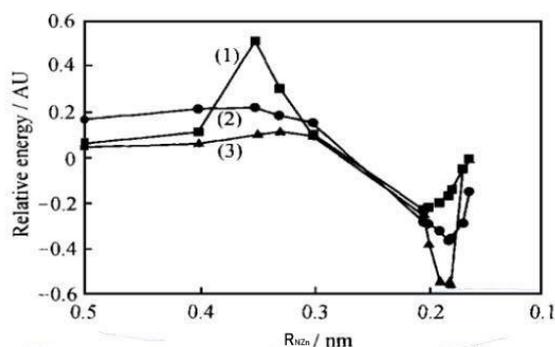


Fig. 4 The potential curves of the chemical adsorption of compounds I, III, V and Fe atoms. Energies are relative to adduct at $R_{Nzn} = 6.0$, absolute energies are -100.7166, -125.4635 and -144.7762 (AU) for compounds I, III and V

3 Discuss

3.1. Molecular structure of ground state

3.1.1. Charge distribution and HOMO

By calculating the net charge distribution of these compounds, it is found that the negative charges of N1 and N3 atoms in the molecules are -0.4555 ~ -0.4370e and -0.3266 ~ -0.2918e. The N Atom in the imidazoline ring is the main contribution to the coefficient of the highest occupied molecular orbital (HOMO), as shown in Table 1. For example, the coefficient of the N1 atom pZ is 0.6744 ~ 0.6391 range. The results show that the chemical adsorption of imidazoline corrosion inhibitor is produced by the interaction of N atom and Zn atom.

3.1.2. Conjugated properties of imidazoline ring

The results show that the inhibition performance of imidazoline is mainly related to the presence or absence of ring. Therefore, the structural properties of the ring are investigated. It is found that the structure of imidazoline ring is almost PLANAR, but not a complete planar ring. The C2 and N3 atoms deviate from the plane by about 15 degrees. In compound I, the two C-N bonds on the ring are 0.1461 and 0.1462 nm, a standard single bond is 0.1460 nm. The non-existence of the p- π conjugation phenomenon of n is shown in Fig. 5a. In Compound II ~

VI, C2=N3 is a double bond, the lone on N1 atom, the pair of electrons can be p- π conjugated with C2=N3, and N1-C2-N3 chain can be p- π conjugated, as shown in Fig. 5b.

Because of the conjugation, the two C-N after optimization are

0.1421 and 0.1301 nm, shorter than the standard single bond 0.146 nm, and longer than the standard double bond 0.128 nm. Due to the delocalization property of the p- π conjugated system, the electrons can be easily transferred and chemically adsorbed on Zn atoms to form a valence bond. Therefore, it can be inferred that the adsorption force of imidazoline compounds with p- π conjugate system to Zn atoms will be stronger than that of compounds without p- π conjugate system. Moreover, with the enhancement of electron donor or conjugation properties, the chemical adsorption force increases.

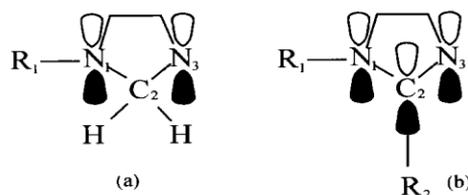


Fig. 5 Conjugated system of compound I ~ VI
 (a) Non-conjugated system of compound I;
 (b) p- π Conjugated System of Compound II ~ VI

3.2. Adsorption potential energy curve

3.2.1. Variation trend of adsorption potential energy curve

In order to investigate the influence of substituents on the chemical adsorption force, the adsorption potential energy curves of Zn atoms and 6 different substituents were calculated by B3LYP method. RN Zn = 0.60nm is used as the initial state to calculate the potential energy curve for relative comparison. According to the calculated adsorption potential energy curve (see the representative curve in Fig. 4), as distance RNZn decreases, energy increases, and the adsorption transition state (TS) is formed at about 0.36nm of RNZn, and then the energy starts to decline. When RNZn is about 0.182nm, the energy reaches a local minimum, forming the adsorption final state (FS). If you go down RN Zn, it's going to go up again. It shows that the imidazoline compound must pass a small energy barrier in the process of chemical adsorption with Zn atom, and finally reach a stable adsorption final state. It is also found that the chemisorption barrier varies with the substituents (see Fig. 4 for details). No p - PI conjugate system of compound I has the highest energy barrier, with p - PI conjugated system and alkyl stupid compounds can II ~ V base is very small, almost as a spontaneous process.

3.2.2. Bond lengths of adsorbed transition states

Careful analysis of the RN Zn distance between TS and FS also reveals interesting problems. It can be seen from Table 2 that the distance between the 6 compounds and Zn atom adsorption transition state RN Zn varies. Among them, compounds I and VI in RN Zn respectively 0.42 and 0.36nm to reach adsorption transition state, and have higher adsorption energy barrier, reflect the two compounds are difficult to form chemical adsorption with Zn atoms transition state. Compound II ~ V in RN Zn for 0.37nm to reach adsorption transition state, adsorption energy barrier is low. From the kinetic point of view, the electron donor group or alkyl aromatics is favorable for chemisorption.

3.2.3. Bond length and adsorption energy of the final adsorption state

When arrived at the end of the adsorption state, compound I RN Zn as 0.204nm, compound II and IV RN Zn is 0.182nm, the rest are 0.180nm. For compound I ~ V, as RNZn is reduced, the absolute value of the corresponding EN Zn and QN Zn generally showed a trend of increase (see chart 2). This not only shows that the coordination bond between compound I ~ VI and Zn is formed, but also has strong chemical adsorption energy. In particular, compounds II ~ VI with P— π conjugated system have a coordination bond length of 0.182nm, the ratio of N to Zn atomic radius is 0.201nm shorter. The results show that the chemical adsorption force between N and Zn is very strong, and the chemical and adsorption force increases with the increase of electron donor or conjugation of substituents. This force can get quantitative (EADS) from the chemical

adsorption, namely no p - PI conjugate system of compound I EADS to a minimum, with p - PI conjugate system of compound II ~ V adsorption can be larger, and from the compound I ~ V, EADS, in turn, increases. A set of parameters RN Zn, EN Zn and QN Zn, which describe the strength of the interaction between N3 and Zn, show that the chemical adsorption force increases in turn, as shown in table 2, but the absolute value of EN Zn and QN Zn of compound VI decrease, this is explained below.

3.3. Effect of substituent on adsorption energy

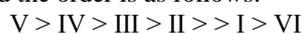
These changes can be explained by the molecular structure of the compounds and the substituent effect. In compound I, due to the absence of p - π system and π delocalized electrons, C2 atoms have no electron donor substituent group and only rely on the lone pair electrons of N atoms to interact with Zn atoms. Chemical adsorption force is weak and energy is high. Therefore, the length of the coordination bond is 0.204 nm, and the EN Zn and QN Zn are smaller. In Compound II ~ VI, because of its p- π conjugation system, not only the lone pair electrons of N atoms interact with Zn, but also the electrons of the conjugation system interact with Zn atoms more easily, forming coordination bonds and stable chemisorption states. For example, the substituent-free compound II RNZn on the C2 atom has 0.182nm, the EADS, ENZn and QNZn are smaller as shown in Table 2. RNZn with electron donor group or substituted aryl Group iii ~ VI is 0.180nm, EADS, ENZn and QNZn were all larger and increased in turn. The effect of the substituents on the stability of the adsorbed state is shown from the thermodynamic point of view. For the compound VI, the electron cloud density of the conjugated system is reduced due to the nitro-electron absorption, which results in the reduction of the adsorption force between N and Zn atoms, and the smaller adsorption force between EADS, EN Zn and QN Zn.

Because the corrosion inhibitor and the metal surface chemical adsorption film more firm, the corrosion inhibition effect is better. Therefore, it can be roughly inferred that the inhibition effects of the above compounds are in the following order: Compounds V > IV > III > II >> I > VI.

4 Conclusion

(1) In imidazoline molecules, the negative charges of N1 and N3 atoms are the largest, and the highest orbital HOMO coefficients are mainly contributed by N atoms in the imidazoline ring, the chemical adsorption of imidazoline corrosion inhibitor is mainly produced by the interaction of N atom and Zn atom.

(2) From the results of calculation, the inhibitive effect of the above compounds can be roughly estimated, and the order is as follows:



(3) Imidazoline ring exists in P— π conjugated system, the introduction of electron donor group or substitution

of aromatic hydrocarbon on the ring can enhance the chemical adsorption force of imidazoline molecule and metal surface and the fastness of the adsorbed film, so as to enhance its corrosion inhibition performance.

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