

Theoretical Investigation of Inhibition Efficiencies of Some Schiff Bases as Corrosion Inhibitors of Aluminum

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The relationships between corrosion inhibition performance of four kinds of Schiff base inhibitors and their molecular electronic properties have been studied by quantum chemistry method at the level of DFT/B3LYP with the 6-31+G (d, p) base sets. The relationships between the corrosion inhibitor efficiency (*IE*) and the result of calculation are discussed using linear regression analysis to determine the most effective parameter on inhibition efficiency, and the regression equations find that the corrosion inhibition performances of these inhibitors have a good linear relationship to total charge of –CH=N- group. In the mean time, the study of the interaction between inhibitors and Al(100) surface shows there are some electrons transferred from inhibitors to the surface, so after adsorption the inhibitor cannot capture electronics from Al and lead corrosion, and it could play a protective effect on the metal surface. Finally, this research might provide a theoretical inhibition performance prediction approach for new homologous inhibitors.

Keywords: modeling studies; corrosion inhibition; Schiff base; inhibition performance prediction

1. INTRODUCTION

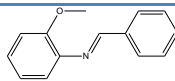
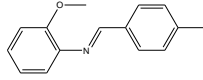
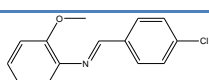
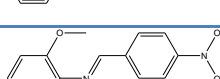
To reasonably apply corrosion inhibitors is a good way to keep metal and metal alloy away from corrosion in environmental medium [1,2]. Corrosion inhibitors, as a protection technique, are widely used in petroleum, chemical industry, construction, etc. Quantum chemical calculation is a good research tool applied in the structure and performance research of corrosion inhibitors to make faster design and evaluation [3]. This method, which is an effective way to make research on complex systems at molecule, atom and even electron level, can provide specific information about molecular structure, electron distribution and adsorbent process of corrosion inhibitors. It is also beneficial for deeply discussing the relationship between the structure and performance of corrosion inhibitors and

studying corrosion inhibition at the micro level. If some relationships between molecular structure and their properties were found, other new kinds of inhibitors could be screened by using quantum calculation methods which will guild a new trend to the molecular design for new corrosion inhibitors [4,5,6].

Many papers have reported that, in order to obtain a good inhibition effect, the inhibitors often had some functional groups[7,8,9] such as nitrogen, oxygen, and sulphur[10,11,12], which could provide electrons. Usually the inhibitors have some rings[7,12,13,14,15] that might get part electrons from these atoms, and have the trend to adsorb on metal surface[8,13], and then form a physical or chemical films to prevent the metal from corrosion, which maybe a general mechanism for the inhibitors[16,17]. Typically, the corrosion inhibitor performance is related with its ability of providing electrons. The more electrons donor ability, the better corrosion performance it will have. If E_{HOMO} value is high, it indicates that electrons in the HOMO orbital have a high energy and electronic ability acting as an electron donor. Likewise, the electric charges are also obviously related with the activity of molecules which maybe responsible for the electrostatic interactions. If the atom or group of the molecule has more negative charge, indicating that they have a good ability providing electrons. These electrons often delocalize to some rings of the molecule, thereby enhancing the inhibition effect.

Along with the enhancement of environmental awareness, due to most corrosion inhibitors contain harmful ingredients^[18]. Some research has been given higher priority to developing new, efficiency, and environmental- friendly corrosion inhibitors [19,20]. Some Schiff bases compounds are arousing more attention owing to their special molecular structure with a $-\text{CH}=\text{N}-$ group [21] and good corrosion inhibition performance to reduce aluminum in acid solution[22]. And some relevant theoretical and experimental studies have been carried out [23,24,25,26,27,28]. The aim of this paper is to study the inhibitive properties of four kinds of Schiff base inhibitors, namely, benzylidene-(2-methoxy-phenyl)-amine, (2-methoxy-phenyl)-(4-methyl-benzylidene)-amine, (4-chloro-benzylidene)-(2-methoxy-phenyl)-amine and (4-nitro-bezylidene)-(2-methoxy-phenyl)-amine. These structures of the compounds investigated are shown in Table 1.

Table 1. Abbreviations and molecular structures of the studied compounds.

Inhibitors	Conformation	Abbreviation
benzylidene-(2-methoxy-phenyl)-amine		Sb-1
(2-methoxy-phenyl)-(4-methyl-benzylidene)-amine		Sb-2
(4-chloro-benzylidene)-(2-methoxy-phenyl)-amine		Sb-3
(4-nitro-bezylidene)-(2-methoxy-phenyl)-amine		Sb-4

Based on theoretical study, through structural parameters such as frontier orbital energy level, dipole moment, charge distribution, interaction with metal surface and other factors, we study on the corrosion inhibition mechanism of this kind of corrosion inhibitors, which will provide theoretical information for distinguishing corrosion inhibition performance and pointing out the direction of predicting and compounding new corrosion inhibitors.

2. CALCULATION METHOD

Density Functional Theory (DFT) [29,30], an economic and efficient quantum chemistry computing method, can provide accurate information of geometrical configuration and electron distribution. It is widely applied in the analysis of corrosion inhibition performance and the interaction of corrosion inhibitors and interfaces. Adopting DFT/B3LYP in Gaussian09 [31], this method conduct geometry optimization and frequency analysis on the objects on the basis set of 6-31+G (d, p) [32,33] for the inhibitors. Making sure that all the structures are minimal points on potential energy surface, we calculate molecular parameters, such as the highest occupied molecular orbital energy (E_{HOMO}), the lowest unoccupied molecular orbital energy (E_{LUMO}), energy gap ($\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$), Mullikan charge population, and the electrons transferred from inhibitor to aluminum surface (ΔN), etc. As for Al atom (metal surface), we use pseudo potential method with LANL2DZ basis set [34,35,36]. In addition, the effect of solvent is using SMD salvation model [37] for all aqueous phase.

3. RESULTS AND DISCUSSION

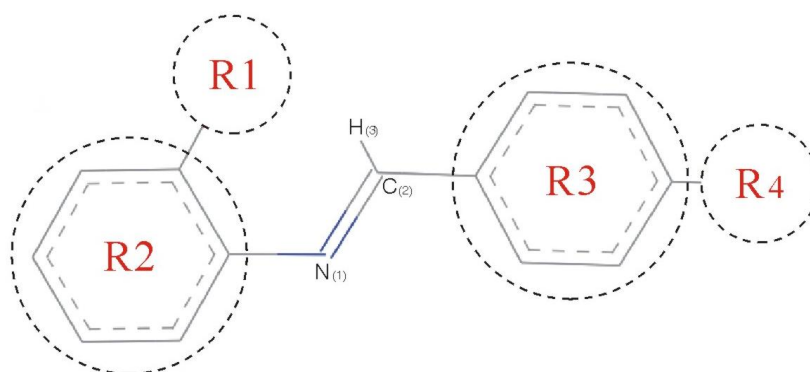


Figure 1. The molecular schematic of inhibitor

The molecular schematic is shown in Figure 1. After DFT B3LYP/6-31+G (d, p) optimization, structural parameters E_{HOMO} , E_{LUMO} , $\Delta E = E_{\text{HOMO}} - E_{\text{LUMO}}$, charges of some atoms and groups, and other quantum chemical parameters are shown in Table 2. $Q_{\text{N}1}$, $Q_{\text{C}2}$ and $Q_{\text{H}3}$ refer to net charge of $\text{N}1$, $\text{C}2$ and $\text{H}3$ on $-\text{CH}=\text{N}-$ group respectively; $Q_{\text{R}1}$ refers to charge of ring $\text{R}1$; $Q_{\text{R}2}$ and $Q_{\text{R}3}$ refer to net charge of C atoms on $\text{R}2$ and $\text{R}3$; $Q_{\text{R}4}$ refers to the charge of $\text{R}4$.

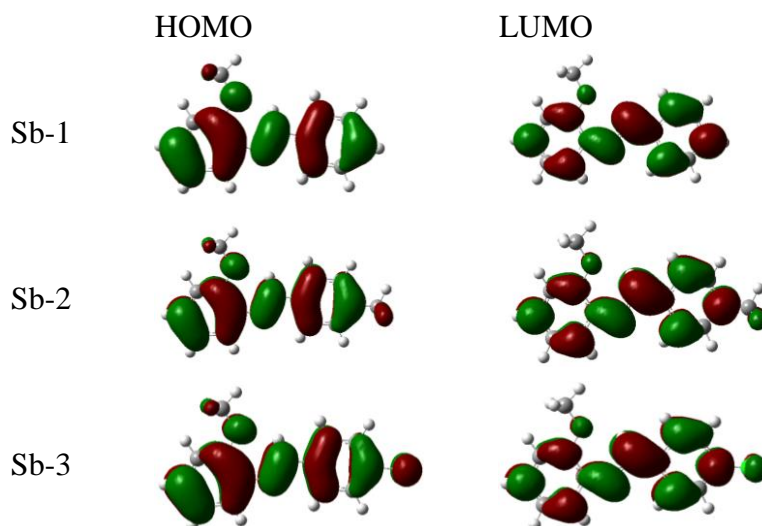
Table 2. Quantum chemical parameters of the studied inhibitors calculated at B3LYP/6-31+G (d, p) level.

Inhibitor	EHO MO	ELU MO	ΔE	ΔN	QN1	QC2	QH3	QR1	QR2	QR3	QR4	IE% ^a
Sb-1	-5.941	-1.895	4.047	2.190	-0.264	0.110	0.173	-0.084	-0.535	-0.861	0.162	96.34
Sb-2	-5.856	-1.823	4.033	2.230	-0.272	0.201	0.170	-0.084	-0.436	-0.752	-0.108	91.16
Sb-3	-5.956	-1.984	3.972	2.309	-0.260	0.190	0.174	-0.080	-0.436	-1.164	0.219	87.63
Sb-4	-6.128	-3.289	2.839	1.914	-0.221	0.254	0.181	-0.075	-0.500	-0.593	-0.447	74.45

^a Exp. value from Ref.[22], the inhibition efficiency (*IE*) for the corrosion of aluminum tested in the 1M HCl with addition of 0.01M of various inhibitor by using weight loss measurement; the energy unit for orbital is eV.

3.1. Frontier molecular orbital characteristic of corrosion inhibitor

According to the theory of quantum chemistry [38,39], the interaction between reactants only happens in frontier molecular orbital. To analyze the adsorption process of corrosion inhibitor we must take HOMO and LUMO of inhibitor molecules into consideration; therein, E_{HOMO} is the measurement of electron donating ability. The smaller E_{HOMO} is, the more stable the electrons are and smaller the electron donating ability is. E_{LUMO} is closely related to molecular electron affinity. E_{LUMO} is small means the electron's system energy decreases much when it enters into this orbital. It also indicates that the molecule can accept electrons easily. $\Delta E = (E_{\text{HOMO}} - E_{\text{LUMO}})$, the orbital energy difference of HOMO and LUMO, is an important stability indicator. The bigger ΔE is, the better the stability is and the worse the activity in chemical reaction. The charge in molecule is the main factor leading to the interaction of electrons. With the charge of atom, it decides many chemical reactions and physical properties [40]. The charge density of atom frontier orbital is of great significance for the study of donor-receptor interaction, as chemical reaction is the charge migration between HOMO and LUMO [39].



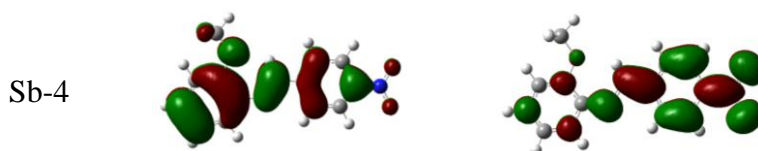


Figure 2. HOMO and LUMO isosurfaces with a value of 0.02a.u. for inhibitors Sb-1,Sb-2, Sb-3 and Sb-4

Figure 2 shows the distribution of HOMO and LUMO of Schiff bases inhibitors. From Figure 2 we can see that all their HOMO and LUMO have the same activity centers. The main delocalization of HOMO orbital is on ring R2, R3 and -N=CH- group. This distribution looks planar and makes the molecule be adsorbed preferentially when adsorption occurs so that empty orbital of metal can easily form coordination bond with the electron provided by inhibitors. At the same time, utilizing anti-bonding orbital on benzene ring, corrosion inhibitors will accept electrons from metal surface and a covalent bond feedback, which helps inhibitor molecules to adsorb firmly on metal surface and effectively hinders corrosion cover on the metal surface.

By conducting unitary or linear fitting with corrosion inhibitor η and frontier orbital energy level, we get parameters such as regression equation, multiple correlation coefficient R, multiple correlation coefficient square R^2 . All these are shown in Table 3.

Table 3. The regression equations of Corrosion inhibition efficiency and their frontier orbital energy

Variable	regression equation		Multiple R	R Square
EHOMO	IE= 505.571+70.042*EHOMO	(1)	0.856	0.733
ELUMO	IE = 115.593+12.545*ELUMO	(2)	0.936	0.877
EHOMO、ELU MO	IE =-51.396-29.712*EHOMO +17.172*ELUMO	(3)	0.943	0.889
ΔE	IE= 31.886+14.912* ΔE	(4)	0.941	0.886

From Table 3 we can find that corrosion inhibition efficiency IE is good closely correlated to frontier molecular orbital E_{HOMO} , E_{LUMO} and ΔE . It can be inferred that the function of corrosion inhibitors are mainly influenced by HOMO and LUMO. From equation (3) we can see that coefficient of E_{LUMO} is positive while that of E_{HOMO} negative, which indicates that HOMO may plays the leading role in corrosion inhibition efficiency because E_{HOMO} is also negative, when it times a negative coefficient and the final result will be positive, which will be favor for the IE value. We can infer that these Schiff base inhibitors adsorbing on metal surface are mainly affected by the following factors: the electrons on HOMO of Schiff base molecules will easily form coordination bond (σ type) with empty orbital of iron. When E_{HOMO} is high (more negative), the electron will be active with strong providing ability; so that it is easy to form coordination bond and corrosion inhibition efficiency is high. As previously mentioned in equation (3), the coefficient of E_{HOMO} is negative, the reason is that N of -N=CH- group could provide lone pair electrons, which will form coordination bond to protect metal surface. At the same time, the π electrons on ring R2 and R3 can form strong coordination bond

with empty orbital metal too, which makes it easy to form protective film on metal surface. In short, the corrosion inhibition performance of Schiff base inhibitors is mainly decided by E_{HOMO} and a little by E_{LUMO} showing positive correlation. Or, we could say they both played a synergistic effect.

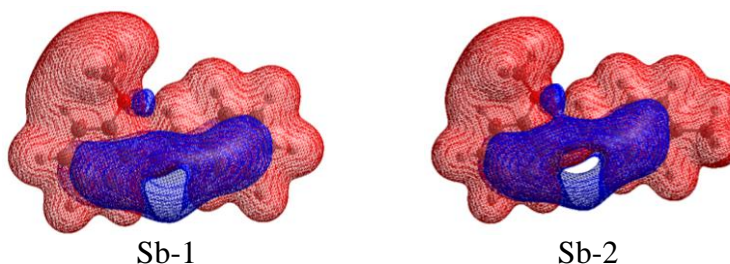
3.2. Correlation between charge and inhibition performance

Table 4 The regression equations of Corrosion inhibition efficiency and different net charges

Variable	regression equation		Multiple R	R Square
QN1	$IE\% = -8.775 - 378.250 * QN1$	(5)	0.920	0.846
QC2	$IE\% = 114.125 - 141.617 * QC2$	(6)	0.902	0.813
(QN1+QC2)	$IE\% = 79.616 - 118.765 * (QN1+QC2)$	(7)	0.973	0.947
QN1, QC2	$IE\% = 42.800 - 235.783 * QN1 - 81.337 * QC2$	(8)	0.997	0.994
(QN1+QC2+QH3)	$IE\% = 99.870 - 114.447 * (QN1+QC2+QH3)$	(9)	0.981	0.963
QR1	$IE\% = -83.050 - 2110.776 * QR1$	(10)	0.965	0.932
QR2	$IE\% = 83.644 - 7.867 * QR2$	(11)	0.041	0.002
QR3	$IE\% = 72.252 - 17.974 * QR3$	(12)	0.464	0.215
QR4	$IE\% = 88.471 + 24.740 * QR4$	(13)	0.806	0.650
(QR1+QR2)	$IE\% = 74.059 - 23.921 * (QR1+QR2)$	(14)	0.126	0.016
(QR3+QR4)	$IE\% = 140.269 + 59.678 * (QR3+QR4)$	(15)	0.925	0.855

We make analysis on linear regression of net charges, such as Q_{N1} , Q_{C2} , $Q_{(\text{N1+C2})}$, $Q_{(\text{N1+C2+H3})}$, Q_{R1} , Q_{R2} , Q_{R3} , Q_{R4} , $(Q_{\text{R1+R2}})$ and $(Q_{\text{R3+R4}})$, etc. and corrosion inhibition efficiency, getting parameters shown in Table 4, such as regression equations, multiple correlation coefficient R, multiple correlation coefficient square R^2 , etc.

From Table 4 we can see that corrosion inhibition efficiency shows close correlation with net charges of atom on $-\text{N}=\text{CH}-$ group (See equations (5)~(9)). As for N1 or C2, the correlation is not so close, from equations (5) or (6) we could find that the multiple correlation coefficient R was about 0.90. But if we took into account them two as a whole, from equation (7) and (8), they had a very excellent correlation with coefficient R of 0.973 and 0.997. meanwhile from equation (8), the coefficient of N1 is about 3 times as that of C2, which infers that the contribution to IE of N1 is much larger than the that of C2, namely, N1 plays a major role in the contribution and it can provide more electrons owing to it has lonely pair electrons.



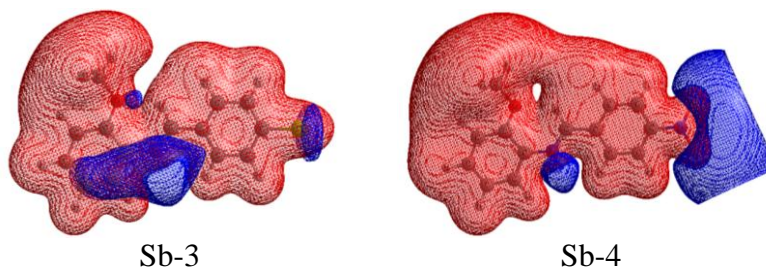


Figure 3. The molecular electrostatic potential surfaces for inhibitors.
 * Isopotential value:0.65 a.u, Blue: negative, Red: positive

In order to further illustrate which part of the inhibitor plays an important role, molecular electrostatic potential surfaces for each molecular are calculated. It can be obviously seen from Figure 3 that center of negative potential concentrate on $-N=CH-$ group, which indicates that the $-N=CH-$ group is a major center for supplying electronic. But there is also a part of the negative charge distribution in the center of the benzene ring R2 and R3 (Sb-1, Sb-2 and Sb-3), which means that when the inhibitor molecules adsorb on a surface (such as Al) benzene ring also plays a synergistic role. As for sb-4, there is a little different, because R4 of Sb-4 is $-NO_2$, which attracts more electrons from the whole molecule and leads to the central charge decline.

3.3. Interaction between Inhibitors and Al (100) surface

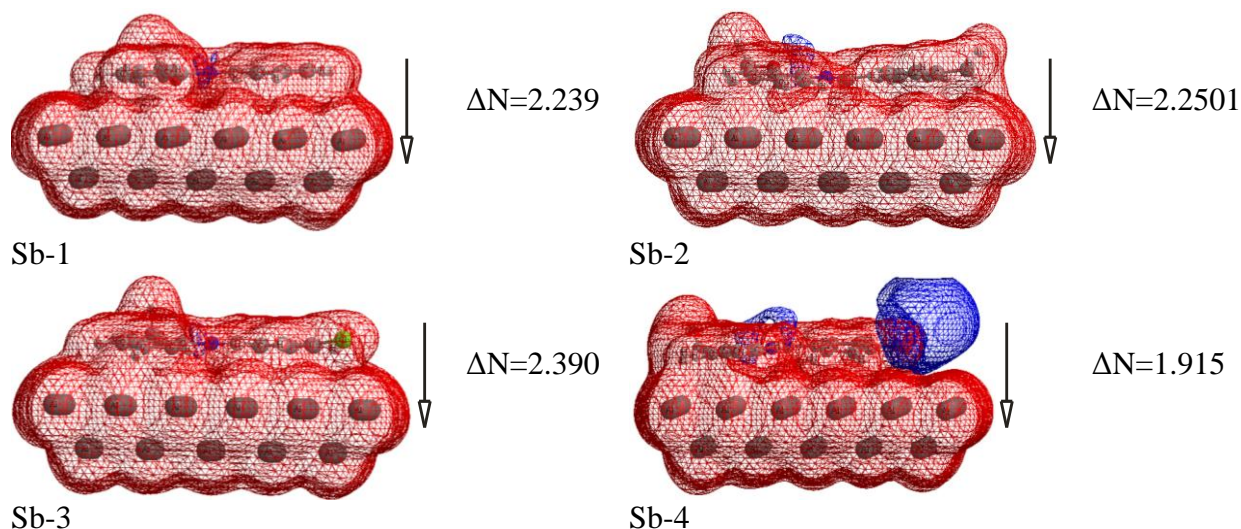


Figure 4. Adsorption configuration and the electrostatic potential surfaces for inhibitor molecules on Al (100) surface
 * Isopotential value:0.65 a.u, Blue: negative, Red: positive

Al (100) surface, as the adsorption surface for corrosion inhibitors, is used as an adsorption surface for inhibitor. We used a two layer of that surface which modeled by clusters of Al_{39} [24,15]. We find that when inhibitor molecules absorb on two-layer Al surface, they tend to keep parallel with metal surface regardless of the initial configuration. They will do micro-vibration at the equilibrium

position. After the quantum calculation for inhibitors adsorption on Al surface, Figure 4 shows the electrostatic potential surfaces and the transferred electrons from inhibitors to Al surface.

From Figure 4 we can find that after the adsorption, there are some electrons transferred from inhibitor to Al surface. Analyzing from the molecular structure after adsorption we can all the inhibitors transfer some electrons to Al surface. But Sb-4 is special in structure as it contains strong electron-withdrawing group $-\text{NO}_2$, which still has more negative charges. Therefore, the numbers of electrons transferred from the molecule to the surface (ΔN) are only 1.915, less than other three inhibitors. This also explains why the Sb-4 has the lowest inhibition efficiency.

3.4. Prediction of the efficiency of some new inhibitors

By quantum chemical study, not only we can understand the mechanism of corrosion and inhibitor adsorption on metal surfaces, determine the merits of corrosion inhibitors, but also the results can help to predict the performance of some homologous corrosion inhibitors, and to provide useful information for the synthesis of these new homologous corrosion inhibitors.

According to the quantum properties of the correlation between the chemical parameters and performances of inhibitors, to play a better inhibition performance, the main structure of corrosion inhibitors should contain $-\text{N}=\text{CH}-$, R2 (benzene) and R3 (benzene) rings. Hence, we design some other homologous Schiff bases corrosion inhibitors just change R4 (Table 5), obtain their quantum chemical parameters using B3LYP/6-31+G(d, p) method and predict their inhibition efficiency (Table 6).

Table 5. Structure of some kinds of homologous inhibitors

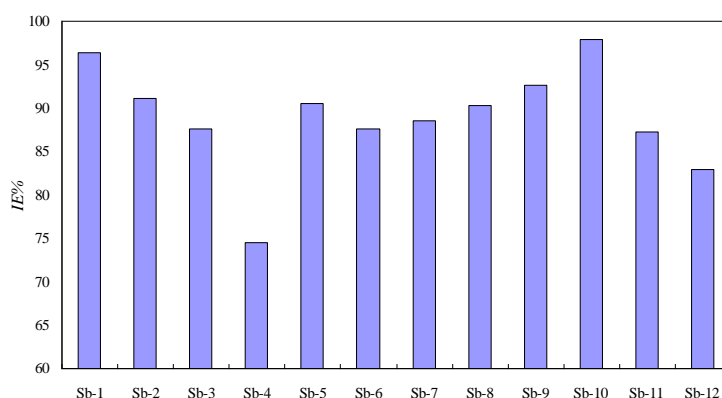
Inhibitor	R1	R2	R3	R4
Sb-5	-OCH3	-Ph	-Ph	-OH
Sb-6	-OCH3	-Ph	-Ph	-SH
Sb-7	-OCH3	-Ph	-Ph	-C2H5
Sb-8	-OCH3	-Ph	-Ph	-Br
Sb-9	-OCH3	-Ph	-Ph	-F
Sb-10	-OCH3	-Ph	-Ph	-OCH3
Sb-11	-OCH3	-Ph	-Ph	-CN
Sb-12	-OCH3	-Ph	-Ph	-CH=CH-CN

It is very easy to find from Table 6 and Figure 5 that Sb-10 has a better performance. But this may be depending on the nature of R4. If R4 have more tendencies to provide electrons, just as for Sb-10, R4 is $-\text{OCH}_3$, which may provide more electrons than others. Hence, $-\text{N}=\text{CH}-$ group will get more negative potential which could benefit for the inhibitor to adsorb on the metal surface and achieve a better inhibition effect.

Table 6. Quantum chemical parameters and prediction of inhibition efficiency for homologous inhibitors

Inhibitor	EHOMO/eV	ELUMO/eV	ΔE /eV	QN1	QC2	QH3	Prediction of inhibition efficiency					Average IE%
							(3)	(4)	(7)	(8)	(9)	
Sb-5	-5.766	-1.751	4.016	-0.279	0.199	0.171	89.867	91.767	89.117	92.179	89.455	90.48
Sb-6	-5.806	-1.830	3.977	-0.140	0.043	0.148	89.704	91.187	91.136	72.203	94.033	87.65
Sb-7	-5.850	-1.828	4.022	-0.269	0.220	0.170	91.033	91.864	85.435	88.121	86.022	88.49
Sb-8	-5.951	-2.000	3.951	-0.255	0.166	0.175	91.068	90.800	90.186	89.223	90.028	90.26
Sb-9	-5.935	-1.883	4.052	-0.262	0.148	0.174	92.616	92.314	93.155	92.332	93.003	92.68
Sb-10	-5.718	-1.761	3.957	-0.271	0.062	0.170	88.261	90.897	104.438	101.442	104.333	97.87
Sb-11	-6.064	-2.394	3.670	-0.235	0.160	0.177	87.660	86.609	88.523	85.011	88.196	87.20
Sb-12	-5.930	-2.562	3.368	-0.244	0.206	0.174	80.807	82.113	84.129	83.385	84.305	82.95

* Formula (3),(4),(7),(8) and (9) presented in Table 3.

**Figure 5.** Comparison chart for some Schiff bases homologous inhibitors and their performance

4. CONCLUSIONS

By using quantum chemistry calculation, we have investigated the relationship between four kinds of Schiff base inhibitors performance and their quantum chemical structure parameters. The detailed studies reveal that corrosion inhibition efficiency shows close correlativity with frontier orbital energy E_{HOMO} & E_{LUMO} , ΔE and Mullikan charge of $-\text{N}=\text{CH}-$ group. The corrosion inhibition performance of Schiff base inhibitors are mainly decided by frontier orbital energy and Mullikan charge of $-\text{N}=\text{CH}-$ group, showing positive correlation. HOMO orbital is mainly delocalizing around two benzene ring and $-\text{N}=\text{CH}-$ group. We also calculate the NBO charges, however the correlation seems be worse. But by analyzing the molecular electrostatic potential surfaces for each molecule, we find that most of negative potential concentrate on $-\text{N}=\text{CH}-$ group and a small part on two benzene rings. $-\text{N}=\text{CH}-$ group plays a main role and R2, R3 play a synergistic role during the process of inhibitor adsorption on a metal surface. Further investigations of the interaction between corrosion inhibitors and Al(100) surface indicate that there are some electrons transferred from inhibitor to surface so as to protect metal not to be corroded. Combining the results of quantum chemistry calculations, the inhibition efficiencies of four inhibitor molecules are the same with the experimental

results. This proves the rationality of evaluating corrosion inhibition performance in theoretical method. Hence, we can theoretically find that the main structure of the inhibitor ($-N=CH-$ group, ring R2 and R3) plays an important for these inhibitors from macro view.

But from this study, we have more important information is that we can design some homologous corrosion inhibitors basing on the following ideas: in the light of the existing structure and properties of corrosion inhibitors, investigate the relationship between quantum chemical structure parameters and inhibition efficiency, find these parameters and main structure which play a major role on the corrosion inhibitor performance, and then change other part of molecular composition to design the new homologous corrosion inhibitors, recalculate quantum chemical structure parameters and use structure-activity relationships to predict the performance of these inhibitors, screen these corrosion inhibitors with excellent performance and design their reaction paths for thermodynamics and kinetics calculations, and finally based on the calculations results to determine whether these selected inhibitors could be synthesized in the laboratory. Hence, the study will be helpful to design and discover some homologous corrosion inhibitors with good inhibition efficiency.

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