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Short Communication

Effect of Schiff's bases Structure on Corrosion Inhibition Efficiency of Copper in Chloride Solutions

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Self-assemble monolayers of different Schiff bases were prepared on a copper surface. EIS, SEM and quantum chemical calculation was used to investigate the relationship between Schiff base structure and corrosion inhibition efficiency. Experimental and computational results showed that the main active regions of these compounds were the characteristic group of imine or methylenimine (- RC = N) and-OH on the benzene rings. The Schiff base reacted with copper to form a chelate covering the surface of copper, which acted as a protective agent for copper, rather than a simple geometric covering effect. The introduction of electron-substituted group into the benzene ring of Schiff base can improve the inhibition efficiency The more the substitution group moved to -C=N-,the more stable the chelate was, and the higher the inhibition efficiency was.

Keywords: Schiff bases; corrosion inhibitors; Self-Assembled Monolayers(SAM);

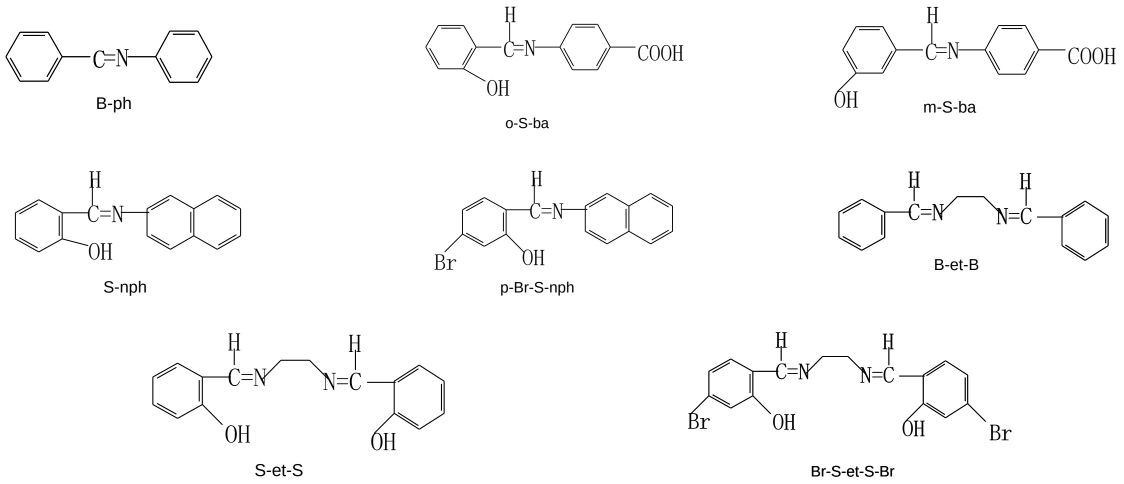
1. INTRODUCTION

The theory and application of corrosion inhibitors are always one of the important topics in corrosion science [1-2]. Because the molecular structure of organic corrosion inhibitors has a decisive influence on its corrosion inhibition performance, their relationship studies have great significance for the selection of corrosion inhibitors [3-5]. Many methods have been developed to study the relationship between corrosion inhibitor properties and molecular structure, such as Linear Free Energy Relationship (LFER), Hemmet Equation [6-7], Hansch Equation [8],and HSAB theory [9].

Self-assembly (SA) is the process of forming ordered molecular films by spontaneous chemical adsorption or chemical reaction [10-11]. Self-assembled monolayers (SAM) can effectively block the transfer of corrosion particles to the metal surface and make the metal substrate free from corrosion [12]. Because of its simple operation and high corrosion inhibition efficiency, this method has attracted scientists' interests in recent years [13].

Schiff bases with special functional groups (-C=N-) can react with copper to form metal chelate and cover the surface of copper, which protect copper [14-19]. In this text, self-assemble monolayers of different Schiff bases were prepared on a copper surface. The relationship between Schiff base structure and corrosion inhibition efficiency was studied by EIS, SEM and quantum chemical calculation.

2. EXPERIMENTAL



B-ph
o-S-ba
m-S-ba
S-nph
p-Br-S-nph
B-et-B
S-et-S
Br-S-et-S-Br

Figure 1. The structure of Schiff bases

2.1. Material

The Capital Normal University provided the Schiff bases. The structure and abbreviations showed in Fig. 1.

2.2 Preparation of electrochemical test system

Conventional three electrodes system was used for electrochemical test, the reference electrode was a Saturated Calomel Electrode (SCE), the auxiliary electrode was a platinum electrode with 1cm^2 and the research electrode was copper electrode. Copper electrode was industrial pure copper rod (mass content> 99%), with 0.3cm diameter, surrounded by epoxy resin.

2.3 Formation of Schiff base self-assembled film

The copper electrodes were polished with metallographic sandpapers and were treated with HNO_3 solution. Then the electrodes were immersed in 1mmol/l Schiff base at room temperature for 30min, the self-assembly films of Schiff base were formed on the copper surface.

2.4 Tests

After film formation, the copper electrodes were removed from Schiff base solution. Then they were eroded in 3%NaCl solution for 30min or 5% HCl solution for 5min f. Lastly the copper electrodes were installed into the test system for performance testing.

The AC impedance was measured by M388 test system of EG&G Company. SEM tests used Hitachi S-570 scanning electron microscope.

3. RESULTS AND DISCUSSION

3.1 SEM test

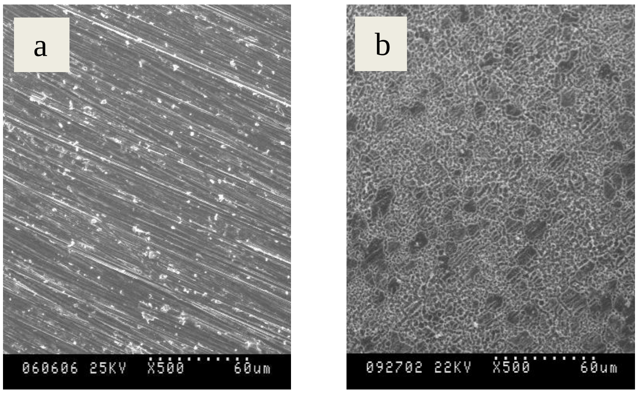


Figure 2. SEM of copper electrode (a) bare copper electrode, (b) Schiff bases modified copper electrode

Fig. 2 showed the SEM photos of B-et-B modified copper electrode and bare copper electrode. As shown in Fig. 2, the morphology of the copper electrode before and after film forming had changed greatly. The copper electrode with film forming was uniform and tight "net" shape, which almost covered the defects on the copper surface. This was the self-assembly film formed by Schiff base on the copper surface.

3.2 AC impedance test

For the convenience of study, the eight Schiff bases in Fig. 1 were grouped: Group A included B-ph, m-S-ba and o-S-ba, Group B included S-nph and Br-S-nph, Group C included B-et-B, S-et-S and Br-S-et-S-Br. Fig. 3 showed Nyquist diagram of Schiff base, A-C group was in NaCl solution and A'-C' was in HCl solution. As shown in Fig. 3a, the half circle appeared in a larger frequency range, which indicated that Schiff base formed self-assembled films on the copper surface and copper corrosion reactions inhibited. The charge transfer reaction played a leading role in the process of metal corrosion. The chord length of the semicircle to the real axis Z' corresponds to the charge transfer resistance R_t [20,21]. For corrosion inhibitor system, R_t reflects the resistance of corrosion inhibitor coating to metal ionization process, or the speed of corrosion reaction. The higher of R_t value was, the greater the resistance of metal ionization process was, and the lower metal corrosion rate was [22].

However, a straight line still appeared in the low frequency region, which was Warburg impedance representing diffusion control [23]. The equivalent circuit showed in Fig. 4, where R_1 was the solution resistance, R_t was the charge transfer resistance at the metal interface, C was the electric double layer capacitance, and W was the concentration polarization resistance or Warburg impedance. Warburg impedance indicated that the electrolyte and corrosion products were diffused among the electrodes and solutions, there were still some defects in the self-assembled monolayers of Schiff bases [24-25].

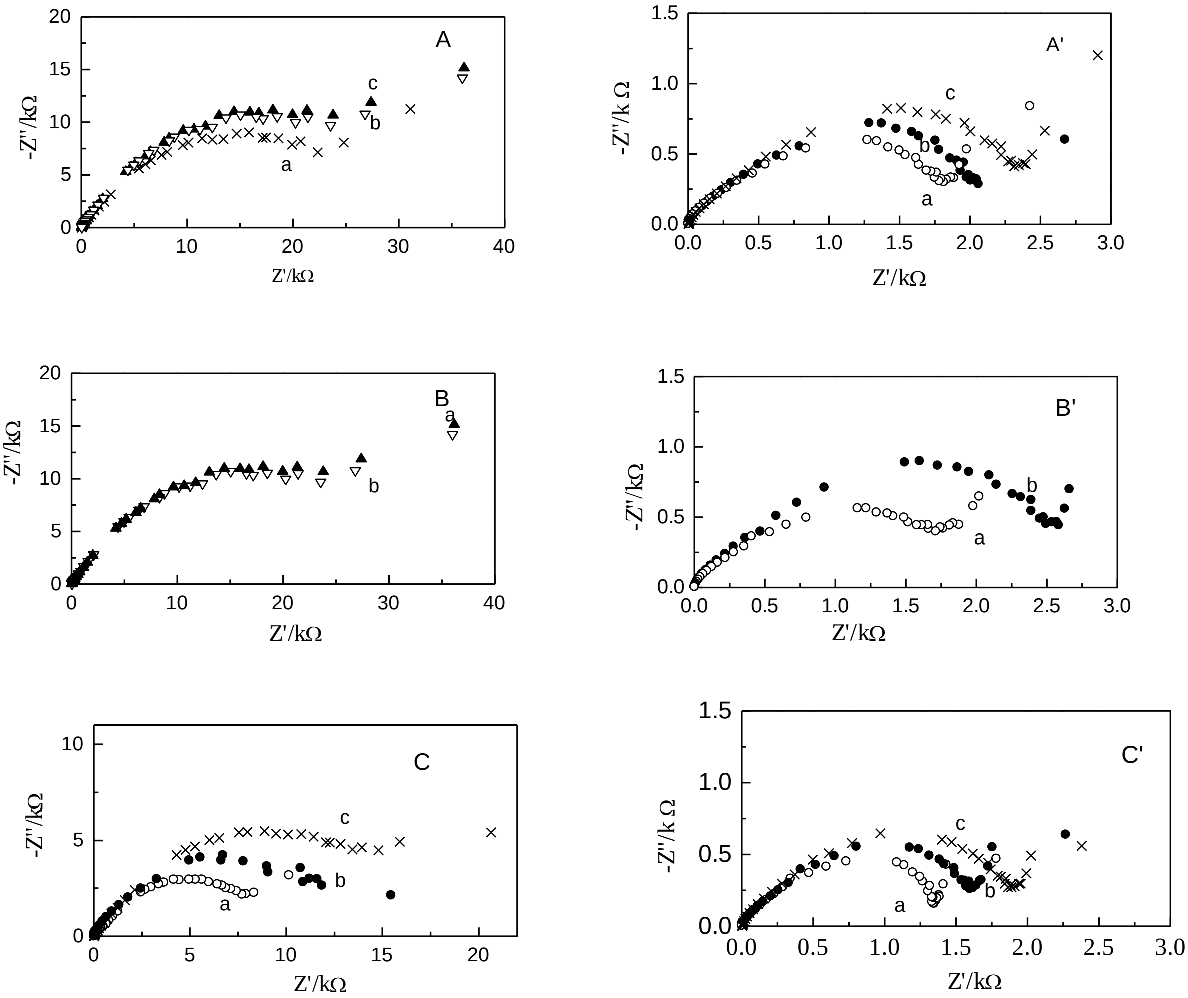


Figure 3. Nyquist diagram of copper electrode formed by different structure Schiff base in NaCl and HCl; A-C in NaCl solution, A'-C' in HCl solution.

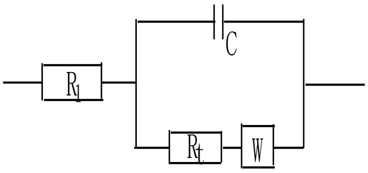


Figure 4. The equivalent circuit of Fig. 3

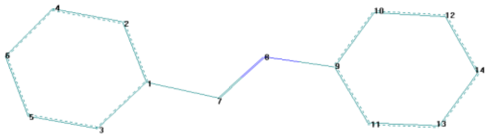


Figure 5. The molecules structure after optimizing

The curves a-c in Fig. 1A and Fig. 1A'were Nyquist diagrams of copper electrodes formed in B-ph, m-S-ba and o-S-ba respectively. The diameter of semicircle (R_t) from a to c increased gradually, which indicated that the inhibition efficiency increasing gradually [22, 26]. Compared with B-ph, m-S-ba and o-S-ba introduced electron donor -OH into the benzene ring, which enhanced the conjugation of the benzene ring and facilitated bonding. Compared with the position of -OH, the -OH in o-S-ba was closer to -C=N-, so the chelate formed with copper was more stable. The changes trend in HCl solution was more obvious than that in NaCl solution, because the corrosion rate of copper in HCl solution was faster than that in neutral NaCl solution.

The curves a-b in Fig. 1B and Fig. 1B' were Nyquist diagrams of copper electrodes formed in S-nph and Br-S-nph respectively. As shown in Fig. 1B and Fig. 1B', the semicircle diameter of Br-S-nph was larger than that of S-nph, which indicated that the corrosion inhibition efficiency of Br-S-nph was higher than that of S-nph. The reason was that Br-S-nph can easily form p-conjugate bonds with benzene rings and form a stable complex with copper by introducing Br substituent on benzene rings [22, 26].

The curves a-c in Fig. 1C and Fig. 1C' were Nyquist diagrams of copper electrodes formed in B-et-B、S-et-S、and Br-S-et-S-Br respectively. As shown in Fig. 1C-Fig. 1C', the diameter of semicircle (R_t) from a-c increased gradually, which indicated that the inhibition efficiency increasing gradually. Compared with B-et-B, two weak electron donor groups -Br were added to the benzene ring of Br-S-et-S-Br, which enhanced the conjugation of Schiff base molecules to form a more stable chelate with copper, so the corrosion inhibition and protection of copper are improved[22,26].

3.3 Relationship between quantum chemical parameters and corrosion inhibition efficiency

When two molecular systems react, it is actually the interaction of two molecular orbitals. The interaction result is that the lower energy reduced and the higher energy increased. According to Fukui Frontier Orbital Theory [27], the intensity of the energy change depends on the degree of overlap of the molecular orbits. The higher the overlap degree is, the more obvious of the energy changes and the more stable compounds are. In general, the higher energy (E_{HOMO}) of the highest occupied orbit (HOMO), the weaker the electron attraction of the nucleus to the HOMO orbit, so these electrons are easier to combine with copper and the inhibition efficiency are higher [28]. The lower the energy (E_{LUMO}) of the lowest empty orbit (LUMO) , the more easily the electron is accepted, so the more easily the feedback bond is formed and the higher the efficiency of corrosion inhibition is[28].

Table 1. The relation between E_{HOMO}/ev,E_{LUMO}/ev and η

Compounds	E_{HOMO}/ev	E_{LUMO}/ev	R_t/kΩ	η	R_t'/kΩ	η'
B-ph	-8.6398	2.0640	17.52	92.57	1.967	91.32
m-S-ba	-8.3658	1.7978	22.25	94.47	2.293	92.58
o-S-ba	-7.4401	2.0376	25.52	95.18	2.632	92.49
S-nph	-7.5261	3.0781	30.12	95.90	2.827	93.99
Br-S-nph	-7.5865	1.7695	31.25	96.06	2.950	94.23
B-et-B	-8.6932	3.0425	10.68	88.5	1.068	84.08
S-et-S	-8.6839	2.6441	12.52	90.17	1.992	91.47
Br-S-et-S-Br	-8.7511	2.2961	18.25	93.26	2.047	91.70

R_t is the charge transfer resistance in 3% NaCl solution; R_t' is the charge transfer resistance in 5% HCl solution; η is the corrosion efficiency in 3% NaCl solution; η' is corrosion efficiency 5% HCl solution

In order to study the relationship between the structure and corrosion inhibition performance of these compounds, the parameters of eight compounds calculated by Gausian98 program. In order to obtain the stable configuration of the molecules, the RHF method and 3-21G basis set used to optimize of the studied object and the optimization results showed in Fig5. In Fig. 5, the number was the location of the element.

It was shown that if the skeleton of the molecule was basically on the same plane, there may be conjugated large π bonds throughout the whole molecular system, that is to say, the whole fraction of the substituent pairs with different properties was introduced into the benzene ring, the charge distribution of the subsystem may have a great influence. The results of the molecular orbit calculation by RHF method and 6-31G base group were shown in Table 1.R_t and R_t' were obtained by the equivalent circuit simulation of Fig. 4 The corrosion efficiency was calculated with $\eta=[(R_t-R_{t0})/R_t]\times100\%$, R_t was the charge transfer resistance of corrosion inhibitor and R_{t0} was the charge transfer resistance of the blank solution [29].The comparison between Br-S-nph and S-nph showed that the E_{HOMO} of Br-S-nph was lower than that of S-nph, which was disadvantageous to electron supply, while E_l was lower than that of S-nph and had strong ability to accept electrons, the experimental results showed that the inhibition efficiency of Br-S-nph was higher than that of S-nph, which indicated that the Schiff base mainly accepted electrons when it formed complex with electrons. The comparison of S-et-S and Br-S-et-S-Br showed that the E_{HOMO} of Br-S-et-S-Br was lower than that of S-et-S, the E_{LUMO} was lower than that of S-et-S, and the inhibition efficiency of Br-S-et-S-Br was higher than that of S-et-S. It also indicated that the Schiff base mainly accepted electrons when it formed complex with copper.

Table 2. The proportion of the main molecules orbit

Compounds		B-ph	m-S-be	Br-S-mph	S-et-S	Br-S-et-S-Br
Orbital content distribution (%)	C_6	12.88	11.37	16.4775	13.7292	10.5120
	C_7	20.14	25.19	15.6469	6.9251	9.2254
	N_8	14.95	13.23	12.1344	9.2245	10.9109
	C_9	7.209	8.105	6.1867		
	C_{10}	7.998		8.0013		
	C_2			9.5801		
	C_3	7.718	8.415		7.8200	
	N_{11}				9.2245	10.9214
	C_{14}	9.967	13.35		7.8208	5.9018
	N_{12}					
	O_{20}					
	O_{21}					
	C_{12}				6.9251	9.2347
	C_{18}				13.7296	10.5216

Table 2 showed the major components and their relative weights of the Schiff base orbitals. As can be seen from table1 and table2, the HOMO and LUMO orbitals of these compounds were linear combinations of the 2P orbitals of the individual atoms. The symmetry was type A and the orbits of LUMO and HOMO were conjugate Π-orbitals. According to the molecular orbital theory, The bonding electrons on Π-orbitals provide electrons to the empty d-orbitals of the metal ligands in the HOMO coordination reaction. Moreover, the higher the energy of HOMO, the easier the reaction was, and the more stable the complex formed. In the LUMO coordination reaction, the empty Π-orbit accepted the metal d-electrons and formed feedback Π-bonds. The presence of Π-bonds and feedback Π-bonds stabilized the presence of Schiff base metal complexes. Moreover, through further analysis of the composition of HOMO and LUMO, we discovered that their molecular composition was mainly concentrated on the imine and -OH of the benzene ring, which further showed that such compounds should be at this site during the coordination reaction. Referring to the photos of Schiff base and copper complex SEM, we initially believed that the complex of this Schiff base and copper was shown in Fig. 5.

As can be seen from Fig.5a and Fig.1A-A', the introduction of -OH into the benzene ring enhanced the conjugation of the benzene ring and can form a more stable complex. The complexes of B-ph with copper were not as stable as the complexes formed by m-S-ba and o-S-ba and the corrosion mitigation efficiency was not as high as the m-S-ba and o-S-ba. The six- ring complex of o-S-ba with copper was more stable than the seven-ring of m-S-ba , therefore, o-S-ba has a strong protection ability against copper and a high corrosion mitigation efficiency. It showed from Fig. 5b. and Fig. 1B-B' that the introduction of the -Br atoms on the Br-S-nph benzene ring improved the conjugation of the benzene ring and improved the protective effect on copper[30].Comparing S-et-S with B-et-B, the introduction of two -OH allowed four Cu (Ⅱ) with two Schiff bases to form a more stable complex in Fig. 5c. Since Br-S-et-S-Br gave two more electron groups -Br compared to S-et-S, the complex formed was more stable and more efficient.

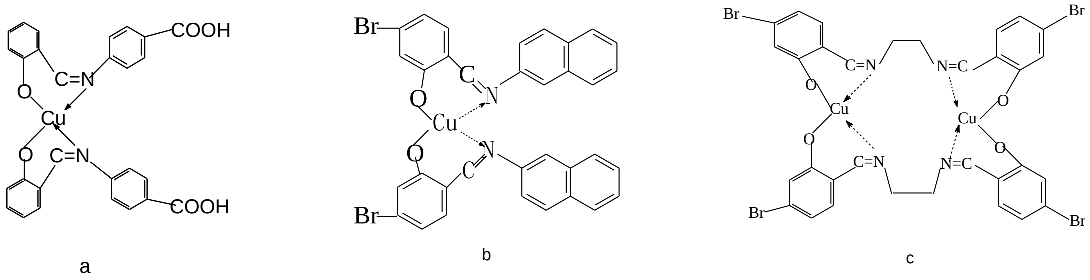


Figure 5. Compounds of schiff bases with copper electrode
a was S-nph with copper, b was Br-S-nph, c was Br-S-et-S-Br with copper

3.4 Relationship between charge distribution and corrosion inhibition

The specific charge distribution in the molecule is an inherent property of the molecule, which determines the physical chemistry property of molecules, so it influences the corrosion inhibition mechanism to some extent. Based on the charge distribution of the inhibitors, we studied the adsorption point and the inhibitors mechanism. In order to study the active region further, the charge distribution was calculated in Table 3.As can be seen from table 3, C_7 and C_9 were the main distribution regions of positive charge, so they should be the main electron accept or regions, and the reaction was mainly concentrated on -C=N- bond. The results were in agreement with those calculated by molecular orbital theory.

Table 3. The distributing of charge density

Compounds	B-ph	m-S-ba	Br-S-nph'	S-et-S	Br-S-et-S-Br
C_2	-.201710	-.212185	-.136969	362868	-.204753
C_3	-.156279	-.156971	367909	-.147432	-.165037
C_6	-.186220	-.214085	-.364788	-.365043	-.187799
C_7	133221	128520	157468	139435	111601
N_8	-.605412	-.601762	-.620285	-.544036	-.532615
C_9	181994	159749	181382	-.116558	-.118952
C_{10}	-.161554	-.106467	-.157651	-.116559	-.118940
N_{11}				-.544036	-.532655
C_{12}	-.211446	-.190117	-.075718	139436	111652
N_{12}					
C_{14}	-.192634	-.122528	-.070327	-.147434	-.165043
C_{18}			-.206891		
O_{20}			-.799133		
O_{21}					

4. CONCLUSION

The relationship between the structural parameters of Schiff bases and their corrosion inhibition properties was studied by AC impedance and quantum chemistry methods. Through the experiment and analysis of molecular orbital energy and charge distribution, it found that the Schiff base compounds should mainly accept electrons during a coordination reaction. The main active regions of these compounds were the characteristic group of imine or methylenimine (-RC=N-) and-OH on the benzene ring. The Schiff base reacted with copper to form a chelate covering the surface of copper, which acted as a protective agent for copper, rather than a simple geometric covering effect. The introduction of electron-substituted group into the benzene ring of Schiff base can improve the inhibition efficiency. The more substitution group moved to -C=N-, the more stable chelate was, and the higher inhibition efficiency was.

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