Benzimidazole Schiff bases as corrosion inhibitors for copper and brass

S. Özbay, T. Yanardağ, S. Dinçer and A. A. Aksüt*

Department of Chemistry, Ankara University, 06100 Ankara, Turkey

*Corresponding author: E-mail: tyanardag@ankara.edu.tr

Abstract
The inhibitive action of newly synthesized ortho-hydroxy Schiff bases of 5-amino-6-nitro-1H-benzimidazole against the corrosion of copper and brass in alkaline medium were studied in respect of their molecular structure using potentiodynamic polarization and electrochemical impedance spectroscopy.

Keywords: corrosion, copper, brass, benzimidazole Schiff bases, inhibitor

1. Introduction
The prevention of corrosion is an important process regarding to wide applications of metals in industry. There are numerous investigation on the treatments of metals with chemical inhibitors for retardation or even suppression of corrosion [1-3]. It is known that among these inhibitors, organic compounds containing one or more heteroatoms in their molecules such as thiazoles, benzotriazoles, imidazoles, benzimidazole derivatives are most effective [4-7]. Corrosion inhibition efficiency of these heterocyclic compounds is explained by the formation of the coordinative bond between heteroatoms of organic compounds containing unshared electron pair and metal atoms which have vacant d orbitals and the corrosion is prevented by the protective film formed on the metal surface. Therefore, the adsorption strongly depends on the electron density at the heteroatoms, naturally on electron-donor or electron-withdrawing properties of functional groups on the organic molecules and molecular structure and steric effects of the inhibitor compounds [8,9].

Recently Schiff bases are reported as a new class of corrosion inhibitors of metals due to the availability of π electrons on the -C=N- double bond which can coordinate with metals to form complexes. However, to the extent of authors best knowledge, the information on the electrochemistry of copper, zinc or brass in alkaline medium in presence of Schiff bases is lacking in the literature [10-13]. In this study, the new Schiff bases of 5-amino-6-nitro-1H-benzimidazole were synthesized and their inhibition efficiencies on the corrosion of copper in alkaline medium have been investigated using polarization and electro chemical impedance spectroscopy.

2. Experimental procedures
2.1. Materials
The working electrodes (WE), copper (99.99 %) and brass (Cu40Zn60), for EIS measurements and potentiodynamic curves were fixed in the teflon tube with adhesive. The surface of the specimens was
polished using emery papers with 1200 grit, etched in 0.15M HCl solution for 20 seconds and rinsed with double distilled water. The reference electrode was a saturated Ag/AgCl electrode and a platinum electrode was used as auxiliary electrode. All the experiments were carried out at room temperature and the solution of tested compounds were prepared at a concentration of 10^{-3} M in ethanol for electrochemical measurements.

The new Schiff bases namely 2-\{[(6-nitro-1H-benzimidazol-5-yl)imino]methyl\}phenol, (BSB) and 1-\{[(6-nitro-1H-benzimidazol-5-yl)imino]methyl\}naphthalen-2-ol (NSB) were synthesized in our laboratory by the condensation reaction of 5-amino-6-nitro-1H-benzimidazole with salicylaldehyde and 2-hydroxy-1-naphthaldehyde \[14, 15\]. Benzimidazole (BI) and 5-nitro-1H-benzimidazole (5-NO_{2}BI) were used to examine the effect of the molecular structure and the substituents on the inhibition efficiencies of new synthesized benzimidazole derivatives. BI and 5-NO_{2}BI were purchased from Fluka and used without further purification. The structural formulas of tested benzimidazole derivatives are given below.

![Structural formulas](image_url)

2.2. Apparatus

The current-time (20minutes), current-potential (1mV/s) and AC impedance curves were performed by constituted CH-Instruments 660B Potentiostat, electrochemical work station of computer programme, BAS disc electrode and Poly Science model 9106 thermostat system.

2.3. EIS measurements

The EIS experiments were performed at open circuit potential of working electrode with voltage perturbation amplitude of 5 mV in a frequency range between 1\times 10^5 – 1\times 10^{-1} Hz. The inhibition efficiency of the benzimidazole Schiff bases is calculated from the formula

IE \% = 1 - (I_{\text{corr}}^{\circ} / I_{\text{corr}})100

where \(I_{\text{corr}}^{\circ}\) and \(I_{\text{corr}}\) are the corrosion current densities in the absence and presence of inhibitors, respectively.

3. Results and discussion

The results obtained using potentiodynamic polarization and electrochemical impedance spectroscopy for copper and brass were interpreted in respect of their molecular structure.

3.1. Polarization curves

Fig.1-4 show the cathodic and anodic polarization curves of copper and brass in 0.4M NaCl+0.1M NaOH solution at 25°C without and with 10^{-3} M of BI, 5-NO_{2}BI, BSB and NSB. Corrosion potential, \((E_{\text{corr}})\), anodic and cathodic Tafel slopes, \((\beta_{a} \text{ and } \beta_{c})\) and corrosion current density, \((I_{\text{corr}})\) were obtained by extrapolation of the anodic and cathodic regions of the Tafel plots and they are given in Table1. The values of corrosion current density, \((I_{\text{corr}})\) of copper and brass in the inhibitor containing solutions were lower than those of the blank. The corrosion current density decreases in the order NBS > BSB > 5-NO_{2}BI > BI for copper and brass. This behaviour of the current density indicates that the new salicylaldimine Schiff base is more efficient inhibitor than the naphthalimine Schiff base for copper and brass in alkaline media.
As seen from Fig.1-4, the inhibition efficiencies (EI %) are increased with the electron density on the molecule for salicylaldimine Schiff base in alkaline media. For the naphthaldimine Schiff base, it is likely that the adsorption on metal surface is prevented by the steric hindrance causing a decrease in the inhibition efficiencies (EI %) for the reported experimental conditions.

Table 1. Electrochemical parameters calculated from polarization measurements on copper and brass in 0.4M NaCl + 0.1M NaOH without and with $10^{-3}$ M of benzimidazole derivatives at 25°C

<table>
<thead>
<tr>
<th></th>
<th>$E_{corr}$ vs Ag/AgCl (V)</th>
<th>$-\beta_c$ (mV dec$^{-1}$)</th>
<th>$\beta_a$ (mV dec$^{-1}$)</th>
<th>$I_{corr}$ (\mu A cm$^{-2}$)</th>
<th>$IE$ %</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Copper</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blank</td>
<td>-0.194</td>
<td>324</td>
<td>286</td>
<td>41.0</td>
<td>-</td>
</tr>
<tr>
<td>BI</td>
<td>-0.180</td>
<td>206</td>
<td>312</td>
<td>1.5</td>
<td>96.0</td>
</tr>
<tr>
<td>5-NO$_2$BI</td>
<td>-0.206</td>
<td>158</td>
<td>127</td>
<td>2.0</td>
<td>95.0</td>
</tr>
<tr>
<td>BSB</td>
<td>-0.153</td>
<td>206</td>
<td>196</td>
<td>3.67</td>
<td>91.0</td>
</tr>
<tr>
<td>NBS</td>
<td>-0.168</td>
<td>219</td>
<td>291</td>
<td>12.0</td>
<td>71.0</td>
</tr>
<tr>
<td><strong>Brass</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blank</td>
<td>-0.437</td>
<td>483</td>
<td>136</td>
<td>118.0</td>
<td>-</td>
</tr>
<tr>
<td>BI</td>
<td>-0.273</td>
<td>206</td>
<td>335</td>
<td>3.0</td>
<td>97.0</td>
</tr>
<tr>
<td>5-NO$_2$BI</td>
<td>-0.344</td>
<td>238</td>
<td>113</td>
<td>4.5</td>
<td>96.0</td>
</tr>
<tr>
<td>BSB</td>
<td>-0.225</td>
<td>187</td>
<td>144</td>
<td>2.97</td>
<td>97.4</td>
</tr>
<tr>
<td>NSB</td>
<td>-0.200</td>
<td>232</td>
<td>116</td>
<td>9.1</td>
<td>92.0</td>
</tr>
</tbody>
</table>

**Fig.1** Polarization curves for copper in 0.4M NaCl+0.1M NaOH solution of BSB

**Fig.2** Polarization curves for copper in 0.4M NaCl+0.1M NaOH solution of NBS
3.2. Electrochemical impedance spectroscopy

The effect of benzimidazole derivatives on the impedance behaviour of copper and brass in alkaline media at 25°C are given in Fig.5-8. The curves of copper in presence of BI and NBS and the curves of brass in presence of BI and 5-NO₂BI show a semi-circle response.

Fig.3 Polarization curves for brass in 0.4M NaCl+0.1M NaOH solution of BSB

Fig.4 Polarization curves for brass in 0.4M NaCl+0.1M NaOH solution of NSB

Fig.5 Current-potential for copper in 0.4M NaCl+0.1M NaOH solution of BSB

Fig.6 Current-potential for copper in 0.4M NaCl+0.1M NaOH solution of NSB

Fig.7 Current-potential for brasss in 0.4M NaCl+0.1M NaOH solution of BSB

Fig.8 Current-potential for brass in 0.4M NaCl+0.1M NaOH solution of NSB
3.2. Molecular structures and inhibiting properties

The coordination properties of benzimidazoles with metals make them efficient inhibitors particularly for copper, zinc and brass in acidic, alkaline and neutral solutions \(^{(16, 17)}\). In this study, benzimidazole Schiff bases having nitro group in their structure were investigated as corrosion inhibitors of copper and brass in alkaline media. Benzimidazole can exist as an anion at pH 13 and its coordination with the metal surface easily leads the formation of protective film at the metal/solution interface.

The inhibition efficiency of benzimidazole derivatives is strongly related to their adsorption properties on metal surface. The molecular structure of benzimidazole Schiff bases manifests two convenient centres to interact with metal surface to provide a coordinate type bond. One of the centres is the unshared electron pairs on the nitrogen atoms and the other is \(\pi\) electrons of the aromatic ring and as well as of the -C=N- group. In alkaline media, increasing of the electron density on the nitrogen atoms could enhance the adsorption and so the inhibition efficiency of the benzimidazole derivatives.

The protective properties of benzimidazoles as inhibitor depend also on the substitution on the ring system. The presence of -NO\(_2\) group which is an electron-withdrawing substituent decreases strongly the electron density of the molecule and the coordination with metal could be hindered. However, it is well known that, depending on its position, the presence of nitro group in benzimidazole molecule causes increased inhibition efficiency for copper \(^{(8)}\). At the same time, these compounds contain -OH group in their structure. -OH group, such as an electron-donating substituent, increases electron density in the molecule and enhances the inhibition properties of the reported benzimidazole Schiff bases. So, it is likely that the protective properties of the substance studies is influenced predominantly by the presence of -C=N- group. The calculated inhibition efficiencies of benzimidazole and its derivatives show that the decreasing effect of the -NO\(_2\) group on the adsorption at the metal/solution interface which is the first step in the mechanism of the inhibitor action is diminished for copper and suppressed for brass under the defined experimental conditions.

An other remarkable result obtained for copper is that the naphthaldimine Schiff base having higher electron density on the molecule manifests weaker inhibition efficiency than that of the salicylaldimine Schiff base. Taking into account the molecular size, it is assumed that the steric hindrance of the naphthalene ring prevents the adsorption on the metal surface. This result suggested that the absorbability of the organic compounds at metal surface depends on the size of molecules as well as on the electron density on the molecules.

4. Conclusions

The efficiencies of newly synthesized benzimidazole Schiff bases as corrosion inhibition for copper and brass in alkaline media have been studied. Results obtained from potentiodynamic polarization and electrochemical impedance spectroscopy indicate that the salicylaldimine Schiff base acts as more efficient inhibitor then the naphthaldimine in the experimental conditions. They exhibit an inhibition efficiency of 91.0 % and 97.4 % for copper and brass respectively.

References

