Investigation of some Schiff bases as acidic corrosion of alloy AA3102

A. Aytac*, Ü. Özmen, M. Kabaşakaloğlu

Department of Chemistry, Faculty of Science, Gazi University, 06500 Teknikokullar Ankara, Turkey

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Abstract

The inhibiting effect of some Schiff bases on the corrosion of AA3102 aluminium in 0.1 M HCl has been studied by means of the hydrogen evolution and electrochemical impedance spectroscopy. The Schiff bases 2-hydroxyacetophenone-etansulphonylhydrazone, Salicylaldehyde-etansulphonylhydrazone, 5-bromosalicylaldehyde-etansulphonylhydrazone and 5-chlorosalicylaldehyde-etansulphonylhydrazone were synthesized from salicylaldehyde and the corresponding amine. The hydrogen evolution tests showed that the corrosion resistance was greatly enhanced in presence of inhibitors. These results were confirmed by the impedance measurements where it was observed that the effect of inhibitor addition appears by an increase in the resistance and by a decrease in the capacity of interface. It is suggested that their effects depend on their concentration and the molecular structures. The maximum inhibition efficiencies were obtained for the 5-bromosalicylaldehyde-etansulphonylhydrazone and 5-chlorosalicylaldehyde-etansulphonylhydrazone by both methods.

Keywords: Aluminium, Corrosion inhibitor, Schiff base, HCl

1. Introduction

Aluminium is extensively used in various industrial operations and the study of its corrosion inhibition in pickling baths is of great importance. Therefore, the inhibition of aluminium corrosion in acid solutions by organic additives has been studied in a considerable detail [1–5]. Organic corrosion inhibitors are an attractive field of research due to its usefulness in various industries. For a given metal, the efficiency of inhibitor depends on the stability of the formed chelate, and the inhibitor molecule should have centers, which are capable of forming bonds with the metal surface via an electron transfer. Generally a strong co-ordination bond causes higher inhibition efficiency, the inhibition increases in the sequence O < N < S < P [6–9].

Several Schiff bases have also been investigated as corrosion inhibitors for different metals and alloys in acidic media [10–12]. Due to the presence of the C=N group, an electron cloud on the aromatic ring, the electronegative nitrogen, oxygen and sulphur atoms in the molecule, Schiff bases should be good corrosion inhibitors [13].

The aim of this study is to investigate the corrosion of aluminium in 0.1 M HCl by four newly synthesized Schiff bases, Table 1, and to observe any relation between molecular structure of these substances and their inhibitive action under various conditions.

2. Experimental

Aluminium specimens of size 2 cm × 0.45 cm × 0.2 cm (compositions: 0.42% Fe, 0.21% Mn, 0.07% Si, 0.01% Ti, 0.01% V as ingredients) were used for hydrogen evolution tests. Prior to each experiment, the surface pretreatment of Al specimens was performed by mechanical polishing (using a polishing machine) of the electrode surface with successive grades of emery papers down to 1200 grit up to a mirror finish. The electrodes were then rinsed with acetone, distilled water and dried at room temperature. For hydrogen evolution test, a special test apparatus was set up. During hydrogen evolution, the changes in the volume of the system were measured as mm of H2O at constant air pressure.
Table 1

<table>
<thead>
<tr>
<th>Structure of Schiff bases Name</th>
<th>2-hydroxyacetophenone-etansulphonylhydrazone (Afesh)</th>
<th>Salicylaldehyde-etansulphonylhydrazone (Salesh)</th>
<th>5-bromosalicylaldehyde-etansulphonylhydrazone (Br-Salesh)</th>
<th>5-chlorosalicylaldehyde-etansulphonylhydrazone (Cl-Salesh)</th>
</tr>
</thead>
</table>

The EIS measurements were carried out in a conventional three electrodes electrochemical cell. The counter and reference electrodes were a platinum plate (2 cm²) and saturated calomel electrode (SCE), respectively. The impedance measurements were conducted after 30 min immersion in experimental solution that ensured a system in equilibrium. The real (Zr) and imaginary (Zi) components of the impedance spectra in the complex plane were recorded using a VoltaLab PGZ 301 EIS voltametry system with an accompanying PC and software.

3. Results and discussion

3.1. Gas evolution tests

Fig. 1 shows the volume of hydrogen evolution of aluminium after 2 h with addition of Schiff bases at different concentrations. All aluminium specimens were put into 30 mL 0.1 M HCl solution at room temperature. It is obvious from Fig. 1 that Br-Salesh is the most efficient inhibitor and reduced the hydrogen evolution compared with other Schiff bases. It is also clear that the corrosion rates decrease with the addition of these inhibitors compared with standard solution (hydrogen evolution after 2 h is 52 mm H₂O for standard solution) and the corrosion rates decrease with increasing inhibitor concentration, except in Cl-Afesh and Br-Salesh.

As an example, Fig. 2 shows the temporal progress of hydrogen evolution for aluminium without inhibitor and with addition of Afesh at different concentration. The slopes of these curves can be taken as the rate of aluminum corrosion (Table 2). All these curves show steady-state hydrogen evolution rate after certain period of time.

The inhibition efficiencies were calculated from the data using formula,

\[
\eta(\%) = \frac{R - R_0}{R_0} \times 100
\]

where \( R \) is the corrosion rate in the presence of inhibitor and \( R_0 \) the corrosion rate without inhibitor. \( R \) and \( R_0 \) values were determined from the slopes of the hydrogen evolution
Table 2

<table>
<thead>
<tr>
<th>Inhibitors</th>
<th>C (ppm)</th>
<th>H₂ evolution rate (mm min⁻¹)</th>
<th>η (%)</th>
<th>Rp (Ω cm²)</th>
<th>η (%)</th>
<th>C (µF cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salesh</td>
<td>10</td>
<td>0.239</td>
<td>70</td>
<td>7.78</td>
<td>76</td>
<td>355</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.205</td>
<td>64</td>
<td>7.35</td>
<td>75</td>
<td>365</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.392</td>
<td>51</td>
<td>7.02</td>
<td>74</td>
<td>380</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>0.348</td>
<td>61</td>
<td>34.2</td>
<td>95</td>
<td>100</td>
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<tr>
<td></td>
<td>50</td>
<td>0.329</td>
<td>59</td>
<td>29.6</td>
<td>94</td>
<td>73</td>
</tr>
<tr>
<td>Cl-Salesh</td>
<td>10</td>
<td>0.228</td>
<td>72</td>
<td>29.4</td>
<td>94</td>
<td>68</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.208</td>
<td>64</td>
<td>23.3</td>
<td>92</td>
<td>86</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.346</td>
<td>57</td>
<td>22.4</td>
<td>92</td>
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<td></td>
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<td>0.337</td>
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<td>27.3</td>
<td>93</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.313</td>
<td>61</td>
<td>20.0</td>
<td>91</td>
<td>67</td>
</tr>
<tr>
<td>Br-Salesh</td>
<td>10</td>
<td>0.091</td>
<td>89</td>
<td>343.0</td>
<td>100</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.121</td>
<td>85</td>
<td>365.2</td>
<td>100</td>
<td>13</td>
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<tr>
<td></td>
<td>30</td>
<td>0.091</td>
<td>89</td>
<td>390.1</td>
<td>100</td>
<td>13</td>
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<td>85</td>
<td>61.0</td>
<td>97</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.251</td>
<td>69</td>
<td>58.2</td>
<td>97</td>
<td>35</td>
</tr>
<tr>
<td>Afesh</td>
<td>10</td>
<td>0.574</td>
<td>28</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.383</td>
<td>52</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.256</td>
<td>68</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>0.222</td>
<td>72</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.239</td>
<td>70</td>
<td>19.3</td>
<td>91</td>
<td>66</td>
</tr>
</tbody>
</table>

Curves for all inhibitors. The Rp was 0.585 mm min⁻¹. For other Schiff bases, (Salesh, Cl-Salesh, and Br-Salesh) there is a certain period of time for hydrogen evolution (Fig. 3). Negative parts of the curves may correspond to oxygen consumption. This time interval increases in the order of, Salesh < Cl-Salesh < Br-Salesh.

This order is also in accordance with the corrosion inhibition efficiency of the Schiff bases. Inhibition efficiencies of other Schiff bases were also calculated from the slopes of the linear part of the temporal progress of hydrogen evolution curves and tabulated in Table 2. Br-Salesh and Cl-Salesh have maximum efficiency at low concentration. The inhibitor efficiency of these Schiff bases decrease at higher inhibitor concentration.

### 3.2. Impedance measurements

Impedance measurements on aluminium electrode in solution with and without Schiff bases at different concentrations with an immersion time of 30 min were performed at open circuit potential (Figs. 4–8).

As we notice from Figs. 6–8, except Afesh, the impedance diagrams show perfect semi-circles indicating a barrier layer formed on the surface and a charge transfer process mainly...
controlling the corrosion of aluminium for Salesh, Cl-Salesh and Br-Salesh at high frequency region and an inductive one at low frequency region. For Afesh, same circular Nyquistic diagram is obtained for high concentration (Fig. 5b). In fact the presence of these Schiff bases enhances the value of charge transfer resistance in 0.1 M HCl solution. The polarisation resistance ($R_p$) and inhibition efficiency ($\eta$ (%)) values of the Schiff bases in 0.1 M HCl solution were given in Table 2.

From the impedance measurements, inhibition efficiencies were calculated using the following expression,

$$\eta \,(\%) = \frac{R_p - R_{p0}}{R_p} \times 100$$

Where $R_p$ and $R_{p0}$ denote polarisation resistance of electrode with and without inhibitor respectively, evaluated from Nyquistic diagrams using circular regression analysis.
Nyquistic diagram obtained in 0.1 M HCl solution. The high frequency capacitive loop could be assigned to the relaxation process in the natural oxide presents on the surface of aluminium sample. Aluminum oxide film is considered to be a parallel circuit of resistor due to ionic conduction in the oxide film and a capacitor due to its dielectric properties [14]. The inductive loop may be attributed to the adsorption of Cl\(^-\) and H\(^+\) ions on the oxide film. These data are consistent with mechanism that proposed the chemisorptions of Cl\(^-\) ions into the oxide surface forming oxide–chloride complex [15,16]. This complex exhibits fast dissolution in the presence of H\(^+\) ion.

Complete inspection of Table 2 reveals that \(R_p\) values decrease while those of \(C_{dl}\) increase with an increase in Br-Salesh and Cl-Salesh concentration. It may result from the fact that adsorption amount and the coverage of these inhibitors are saturated on the surface at low concentration. At higher concentrations of the Schiff bases some desorption occur. The Schiff bases form of the chelate complex withbare aluminium surface at higher concentrations.

The presence of the inhibitor does not alter the shape of impedance spectra of Salesh, Cl-Salesh and Br-Salesh suggesting similar mechanism for the metal dissolution in 0.1 M HCl solution. The same Nyquistic impedance profile is obtained at 50 ppm of Afesh. For lower Afesh concentrations, Nyquistic diagrams show Warburg impedance behaviour, which can be attributed to diffusion controlled dissolution process.

Adsorption of these Schiff bases probably occur on bare surface with oxygen consumption since at the beginning of the hydrogen evolution measurement the volume of the corrosion system decrease at constant pressure. After the consumption of dissolved oxygen in the solution, the hydrogen evolution begins slowly. For maximum adsorption efficiency there must be optimum concentrations for Schiff bases and dissolved oxygen in acidic solution. The Schiff bases form of the chelate complex with bare aluminium surface at higher than optimum concentration. According to the structures of these Schiff bases convenience of complex formation is increased in the order of Afesh > Salesh > Cl-Salesh > Br-Salesh and is in the reverse order of inhibitor efficiency.

In order to get a better understanding of the electrochemical process on the metal surface, adsorption characteristics at room temperature were also studied for Salesh, Afesh, Br-Salesh and Cl-Salesh. It is well known that this process is closely related to the adsorption of the inhibitors molecules [17,18] and the adsorption depends on the molecular structure [19,20].

Fig. 9 illustrates the variations of inhibition efficiency versus the logarithm of the concentrations of Schiff bases. The plots for Afesh and Salesh have S shaped adsorption isotherms. Therefore these Schiff bases seem to function as inhibitor by being adsorbed on the metal surface. This adsorption can be stabilized by participation of lone pair electrons of sulphur, imine nitrogen and \(\pi\) electrons of aromatic ring. Electronegative bromine and chlorine atoms facilitate the adsorption of molecule on the aluminium surface. Dissolved oxygen molecules play synergetic effect on the adsorption of Schiff bases.

4. Conclusions

- The protection ability of these Schiff bases, is given in the order of Afesh < Salesh < Cl-Salesh < Br-Salesh. Cl-Salesh and Br-Salesh are the most effective ones, since they have electronegative atoms as chlorine and bromine as a para substituent on phenol ring.
- When a phenol has chlorine and bromine substituent in para position, oxygen molecule as a radical is tied to the hydroxyl group of benzene ring and then Cl or Br phenolic radical is formed. Resonance in these adsorbed phenolic radicals makes stabile radical structure and electron barrier against dissolution of aluminium atoms.
- The most effective inhibitor is Br-Salesh since it has higher molecular weight than Cl-Salesh. Dispersion forces assist to adsorption in addition to other adsorption forces. Methyl group on Afesh makes steric hindrance on the adsorption of these molecules on the surface.

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References