



# EUROCORR 2008

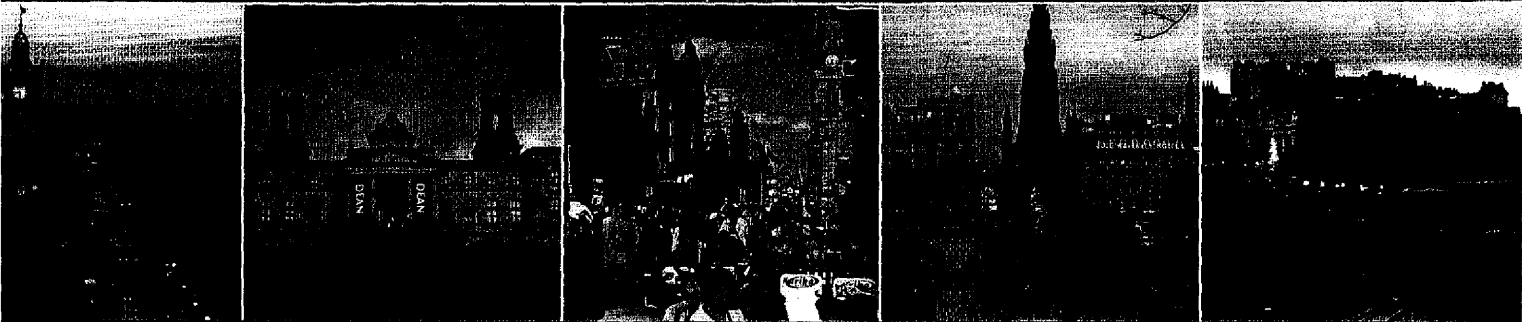
THE EUROPEAN CORROSION CONGRESS

»Managing Corrosion for Sustainability«



**EFC**

European Federation of Corrosion · Event No. 299



7 - 11 September 2008

Edinburgh International Conference Centre · United Kingdom

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## PROGRAMME



**Bodycote** TESTING GROUP

Monday, 8 September 2008

09:00 - 09:15	Opening Session - S.B. Lyon University of Manchester/UK; M. Schütze, DECHEMA e.V., Frankfurt am Main/D	
09:15 - 09:30	Welcome Address: Michael Russell MSP, Minister for Environment, The Scottish Parliament, Edinburgh/UK	
09:30 - 09:45	Cavallaro Medal Award Presentation	
09:45 - 10:30	<b>INVITED PLENARY LECTURE</b>	
10:30 - 11:00	<b>Coffee Break</b>	
	<b>Chair(s)</b>	<b>Chair(s)</b>
10:30 - 11:00	Stability of Al <sub>2</sub> O <sub>3</sub> surface films on aluminium and corrosion protection in aggressive media	P. Marcus, Ecole Nationale Supérieure de Chimie de Paris/F; J.M.C. Mol, Delft University of Technology/NL
11:00 - 11:25	Development and validation of a fast scanning technique for anisotropic impurity detection	<b>Monitoring stress corrosion cracking</b> S. Holzleitner, Materials Center Leoben Forschung GmbH/A; G. Mori, University of Leoben/A; S. Eglisäer, Böhler Edelstahl GmbH & Co. KG, Kapfenberg/A
11:25 - 11:50	Online wavelet diagnosis of electrochemical noise for evaluation of cathodic lining concentrations	<b>Factors affecting SCC susceptibility of modified 13Cr martensitic stainless steels</b> P. Hernandez Hernandez, Instituto Mexicano del Petroleo, Distrito Federal/MEX; R.A. Cottis, University of Manchester/UK; R.C. Newman, University of Toronto/CDN
11:50 - 12:15	Stability of passive and stable oxide forming films (FEA) of the corrosion products on steel in carbon dioxide water circuits	<b>Slip-dissolution model of stress corrosion crack growth and possibilities of its application for evaluation of stress corrosion cracking susceptibility of duplex stainless steels in hydrogen sulfide-chloride environments at 120°C</b> B. Eremias, V. Janik, V. Chai, E. Kalabisova, SVUOM Ltd., Prague/CZ
12:15 - 12:40	Surface analytical characterization of alkyl-diphosphate thin layers on passive metal films	<b>Corrosion fatigue of solution annealed austenitic stainless steels</b> B. Sonnelitner, G. Mori, M. Parzenböck, University of Leoben/A; R. Fluch, S. Eglisäer, Böhler Edelstahl GmbH & Co. KG, Kapfenberg/A
12:40 - 14:00	<b>Lunchtime</b>	
	<b>Chair(s)</b>	<b>Chair(s)</b>
14:00 - 14:25	On passivity of iron in anoxic sodium methanesulfonate, sodium sulfate and their combinations with sodium chloride	P. Marcus, Ecole Nationale Supérieure de Chimie de Paris/F; J.M.C. Mol, Delft University of Technology/NL
14:25 - 14:50	Transformation of iron in the presence of mangrove ( <i>Rhizophora apiculata</i> ) tannins and phosphoric acid	<b>Spectro-electrochemical studies of surface treated metal / polymer interfaces upon exposure to an electrolyte solution</b> M. Öhman, D. Persson, Swerea KIMAB, Stockholm/S
14:50 - 15:15	Synthesis and electrochromic properties of ZnO system	<b>A high resolution X-ray photoelectron spectroscopy study of chromium conversion coatings and compounds</b> R. Chapaneri, G.W. Critchlow, G.D. Wilcox, I. Sutherland, Loughborough University/UK; G. Beamson, Daresbury Laboratory, Warrington/UK; A. Chojnicki, T. Pearson, T. Rowan, MacDermid PLC, Birmingham/UK
15:15 - 15:40	Use of flavonoid plant extracts on the corrosion behaviour of duplex stainless steels	<b>Stainless steel passive film modification by electrochemically cerium insertion</b> Q. Lavigne, C. Alemany-Dumont, B. Normand, INSA Lyon, Villeurbanne/F; P. Delichère, UCLB - CNRS, Lyon/F
15:40 - 16:15	<b>Coffee Break</b>	
16:15 - 16:40	Synthesis of Schiff bases as a potential corrosion inhibitor of aluminium	<b>X-ray photoelectron spectroscopy study of oxide film formed on Ni-base alloys in pressurized water reactor primary conditions</b> L. Marchetti, S. Perrin, O. Raquet, F. Misergue, CEA Saclay, Gif-sur-Yvette/F; M. Pijolat, Ecole Nationale Supérieure des Mines, Saint Etienne/F
16:40 - 17:05	Mangrove ( <i>Rhizophora apiculata</i> ) tannins as a potential corrosion inhibitor for aluminium in acidic medium	

# Synthesised Schiff bases as a potential corrosion inhibitor of aluminium

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## Abstract

The use of inhibitors for the protection against corrosion in acidic media such as nitric acid, sulfuric acid and hydrochloric acid is widely reported. Schiff bases, a group of compounds containing nitrogen atoms were found to be efficient inhibitors for corrosion in acidic media. Some research work revealed that the inhibition efficiency of Schiff bases was found to be greater than their precursor, amines and aldehydes.

In this study, the corrosion inhibition of aluminium by the synthesised Schiff's bases in acidic solution (HCl) was investigated by weight loss measurements and potentiodynamic measurement. The synthesised Schiff bases used in this study were as follows: N,N'-(4-hydroxybenzylidene)-m-phenylenediamine (1), N,N'-(2-hydroxy-3-methoxybenzylidene)-m-phenylenediamine (2), (*E*)-4-bromo-2-((4-bromophenylimino)methyl)phenol (3) and (*E*)-4-bromo-2-((pyridine-2-ylimino)methyl)phenol (4). All the Schiff bases obtained were characterised using FTIR, <sup>1</sup>H and <sup>13</sup>C NMR. Results of inhibition efficiencies observed from these two methods are in good agreement and have been found to be dependent on the concentration of Schiff bases. It was observed that the inhibition efficiency of all Schiff bases increased with increasing concentrations of all Schiff bases, indicating their potential corrosion inhibitor of aluminium.

## 1. Introduction

Aromatic or heterocyclic aromatic compounds containing nitrogen were used as corrosion inhibitors in acidic media (Gamma, 1993, 1995). Schiff bases, an example of compound containing nitrogen which can be derived from the reaction of an amine and a ketone or aldehyde are well known organic inhibitors (Hosseini, 2003; Yurt et al., 2004). Behpour et al. reported the presence of -C=N- group in the Schiff base molecules was the reason in the inhibition efficiency. (Behpour et al., Li et al., 1999) Al-Douh et al. prepared benzylidene compounds by the acid-catalyzed reaction of aromatic aldehydes and amine compounds in boiling absolute ethanol. Those products were re-crystallized from ethanol and was believed to follow tetrahedral mechanism (Al-Douh et al., 2004).

The aim of this present study was to examine Schiff bases compound 1-4 as an inhibitor for the corrosion of Al in 0.5 M H<sub>2</sub>SO<sub>4</sub>, on the basis of weight loss and

potentiodynamic measurement data. The result of this study may be useful to researcher attempting to gain more understanding of the corrosion activity of Schiff base compounds.

## 2. Experimental details

### 2.1 Synthesis of Schiff Bases

The molecular structures of the examined Schiff bases are shown in Fig. 1. Studied Schiff bases were synthesized according to published method (Al-Douh et al., 2004 and Hadjoudis et. al.,1987) with a slight modification. Briefly **1** and **2** were prepared by condensation of benzene-1,3-diamine with 4-hydroxy benzaldehyde and 2-hydroxy-3-methoxy benzaldehyde respectively. While **3** and **4** were prepared by condensation of 5-bromosalicylaldehyde with 4-bromoaniline and 2-aminopyridine, respectively. All chemicals used were analytical reagent grade (Merck) and were used without further purification. All the compounds were characterized by FTIR, <sup>1</sup>H-NMR and <sup>13</sup>C-NMR and were consistent with the structure reported earlier (Al-Douh et al., 2004 and Hadjoudis et. al.,1987).

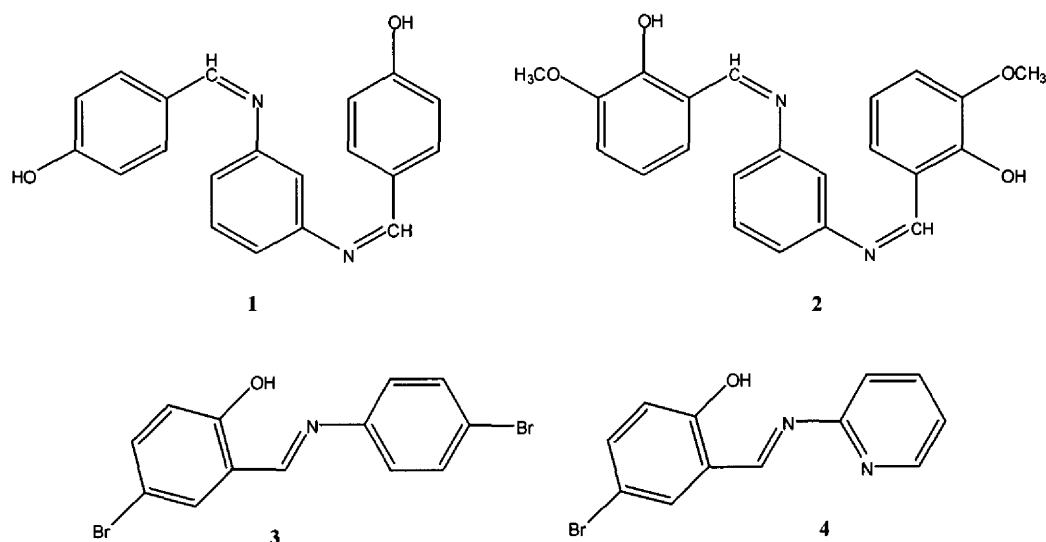


Figure 1 : Schiff bases, *N,N'*-(4-hydroxybenzylidene)-*m*-phenylenediamine (**1**), *N,N'*-(2-hydroxy-3-methoxybenzylidene)-*m*-phenylenediamine (**2**), (*E*)-4-bromo-2-((4-bromophenylimino)methyl)phenol(**3**), (*E*)-4-bromo-2-((pyridine-2-ylimino)methyl)phenol (**4**)

## 2.2 Measurement of Corrosion Inhibition

### 2.2.1 Weight Loss Measurement

Weight loss measurements were performed using rectangular aluminium specimens, of size 1.5 cm × 3 cm. The samples were first polished to a mirror finish using 600, 800, 1000 and 1200 grit emery paper, washed with double distilled water and dried at room temperature. The mass of the samples were then determined using an analytical balance. The samples were immersed for a period of 24 hours in 10 mL 0.5 M HCl solution containing various concentrations of the studied inhibitors. Inhibitor concentration were chosen as 0.1, 0.2, 0.3, 0.4 and 0.5 gL<sup>-1</sup> in 25% ethanol at room temperature. The samples were then rinsed with distilled water, degreased with acetone and finally rinsed with distilled water. The samples were dried at room temperature. The mass of the samples were determined. The inhibition efficiency, % IE were calculated in the classical way as

follow (Hosseini *et. al.*, 2003):

$$\%IE = \frac{W_0 - W}{W_0} \times 100$$

where  $W_0$  and  $W$  are weight loss observed in the absence, respectively, in the presence of inhibitor. All determinations were made in triplicate.

#### 2.2.1.1 Working Electrode

The employed working electrodes were prepared from a aluminium plate with the chemical composition: 0.24% Fe, 0.47% Ag, 3.61% C, 11.61% O and 84.08% Al. The metal plate was cut as square specimens having 9 cm<sup>2</sup> area. The metal plate was then polished to a mirror finish using 600, 800, 1000 and 1200 grit emery paper. The electrodes then degreased in acetone and double distilled water.

### 2.2.2 Polarization Measurement

Polarization measurements were carried out using a PC controlled Volta Lab, PGP 201 system with Voltmaster 4 software. A platinum and a saturated calomel electrode were used as the auxiliary and reference electrode, respectively. Working electrode was first immersed into the 50 mL 0.5 M HCl solution containing various concentrations of the studied inhibitors as mentioned in section 2.2.1 for 30 min to establish a steady state open circuit potential. Potentiodynamic polarization studies was performed with a scan rate of 0.5 mV/sec in the potential range from -1000 to -100 mV. The inhibition efficiency was calculated using the relation as follows (Behpour *et. al.*, 2007):

$$\%IE = \frac{I_{corr} - I_{corr(inh)}}{I_{corr}} \times 100$$

where  $I_{corr}$  and  $I_{corr(inh)}$  are corrosion current density observed without and with inhibitor respectively.

### 3. Result and discussion

#### 3.1 Weight Loss Measurement

When Al was immersed with 0.5 M HCl, it will suffer a weight loss. The evaluation of inhibition efficiency (%IE) was performed through weight loss experiments and was calculated by using equation in part 2.2.1. The effect of absence and presence of various inhibitor concentrations on the inhibition efficiency for aluminium in 0.5 M HCl are shown in Table 1 and 2. Generally, the result shows that the efficiency of all the compounds increases with increasing inhibitor concentration. It should be noted that the increased of inhibition efficiency of **2** and **3** is rather small as compared to **1** and **4**. However **2** and **3** are shown higher inhibition efficiency among examined inhibitors. The chemical structure of the organic molecule would affect the adsorption process in the adsorption mechanism of inhibitor onto the metal surface (Emregül, 2006). The structure of compound **2** is slightly the same as compound **1**, but in term of the inhibition result, it shown higher inhibition efficiency than compound **1**. This is attributable to the presence of an electron releasing group (-OCH<sub>3</sub>) which increases the inhibitor rate by increasing the electron density (Emregül, 2006). While

compound **2** shows higher inhibition efficiency than compound **3**. The more aromatic ring in compound **2** is assumed to affect the inhibition rate of **2**, since the adsorption of the molecules on the surface by interaction with  $\pi$  electrons of the aromatic ring (Behpour et al., 2008). The bigger the size of molecules the more effective adsorption and subsequently higher inhibition efficiency. This phenomenon results the higher inhibition efficiency of **2**. Behpour et al. was reported the same observation in their corrosion study (Behpour et al., 2008).

The other observation was found for compound **3** and **4**. Even though their structures are slightly the same, but compound **4** shows higher inhibition efficiency than compound **3**. The difference in inhibition between **3** and **4** arises due to the presence of  $\pi$  electron deficient ring (i.e. pyridine) in **4** as a substituent. The presence of pyridine in **4** as a substituent causes decrease of electron density of C=N group which gives a less efficient protection action of aluminium surface than **3** (Yurt *et. al.*, 2004). Substitution of two bromine atoms on the benzene ring affects the inhibition efficiency of compound **3** and **4**. This result shows that Br atom on benzene ring in this molecules are the most probable additional centres of adsorption. Thus inhibitor functions of **3** are related to a specific adsorption mechanism that depends on the magnitude of negative charges on the Br atom.

Table 1: Data of inhibitor concentration on inhibition efficiency of Schiff bases **1** and **2** for aluminium in 0.5M HCl (weight loss measurement)

Concentration (M)	Inhibition efficiencies (%IE) (1)	Inhibition efficiencies (%IE)(2)
Blank	-	-
$3.0 \times 10^{-3}$	17.56	82.88
$6.0 \times 10^{-3}$	25.45	91.62
$9.0 \times 10^{-3}$	29.75	89.98
$1.2 \times 10^{-2}$	34.23	89.98
$1.5 \times 10^{-2}$	39.25	88.16



Table 2: Data of inhibitor concentration on inhibition efficiency of Schiff bases **3** and **4** for aluminium in 0.5M HCl (weight loss measurement)

Concentration (M)	Inhibition efficiencies (%IE) ( <b>3</b> )	Inhibition efficiencies (%IE)( <b>4</b> )
Blank	-	-
$2.8 \times 10^{-4}$	81.82	11.89
$5.6 \times 10^{-4}$	85.31	13.99
$8.4 \times 10^{-4}$	88.11	28.67
$1.1 \times 10^{-3}$	89.04	28.44
$1.4 \times 10^{-3}$	89.51	31.00

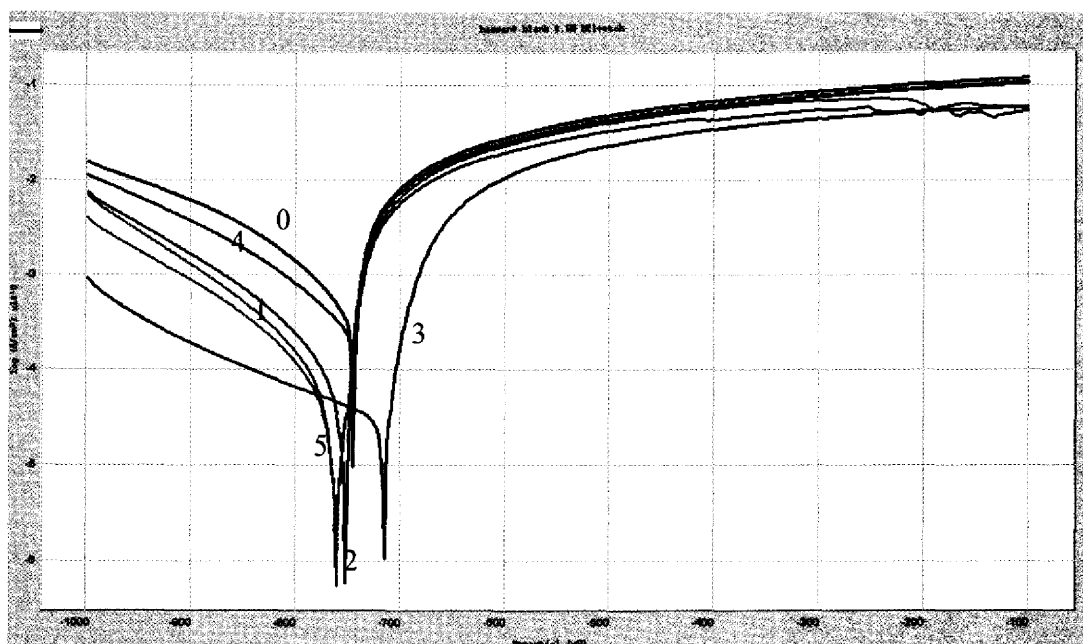
### 3.2 Polarization Measurement

The electrochemical parameters associated with polarization measurements and the inhibition efficiency (%IE) at different concentrations are listed in Table 3-4, where  $E_{corr}$ ,  $R_p$ ,  $I_{corr}$ ,  $B_a$  and  $B_c$  are the corrosion potential, polarization resistance, corrosion current density, anodic and cathodic Tafel slopes, respectively. The effect of inhibitor concentration on the inhibition efficiency of the two Schiff bases for aluminium in 0.5 M HCl in the absence and presence of various inhibitor concentrations of **1-4** are shown in Figs 3-6. These Figures shows the influence of various concentrations of compounds **1-4** respectively on the polarization behavior of aluminium in 0.5 M HCl. The curve represent results the corrosion current density which has been compared with the blank curve. The addition of Schiff base **1** to acid media will affect both the cathodic and anodic parts of the curve, where the corrosion potential shifted to positive and negative direction, therefore this compound behaved as mixed anodic-cathodic inhibitors.

The other Schiff bases **2-4** shows a different observation, where corrosion potential shifted to negative direction more likely. This shows that the effect of inhibitors on the cathodic reaction is more observable on the anodic reaction. It is also observed that, the cathodic curves show lower current density in the presence of Schiff bases than those recorded in the solution without the inhibitor while the anodic curves did



not show any changes in the current density in the presence of Schiff bases 2-4. This behavior indicated that those compounds influencing the cathodic reaction of corrosion process. Therefore, these compounds could be classified as cathodic inhibitor.



Legend:

1 (blank 0.5M HCl), 2 ( $3 \times 10^{-3}$  M), 3 ( $6 \times 10^{-3}$  M), 4 ( $9 \times 10^{-3}$  M), 5 ( $1.2 \times 10^{-2}$  M)  
6 ( $15 \times 10^{-3}$  M)

Figure 2: Polarization curves for the aluminium in 0.5M HCl with and without various concentrations of compound 1

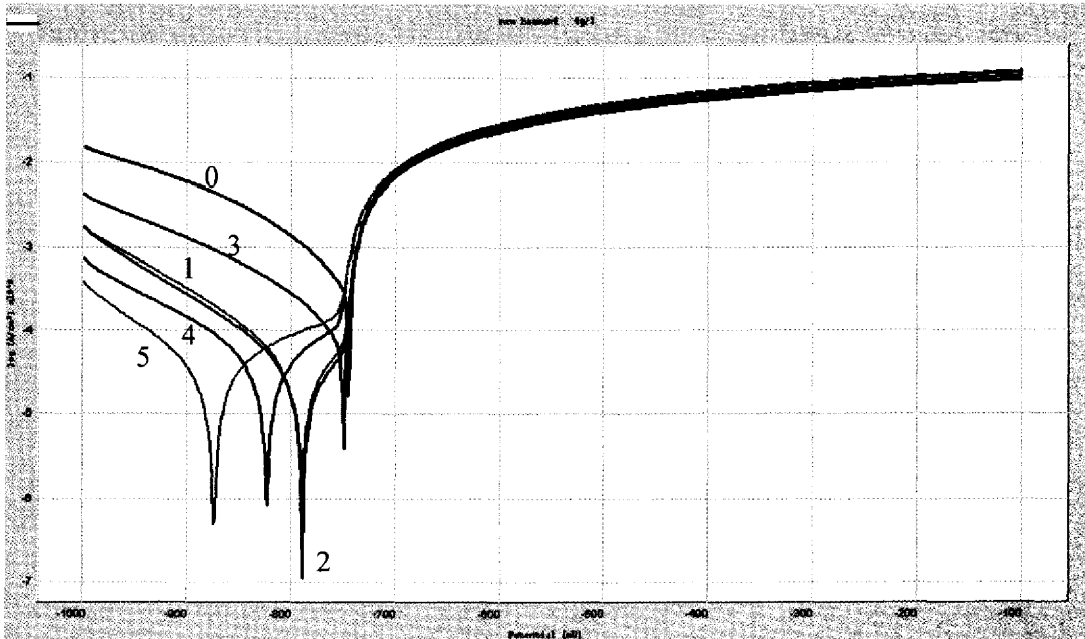
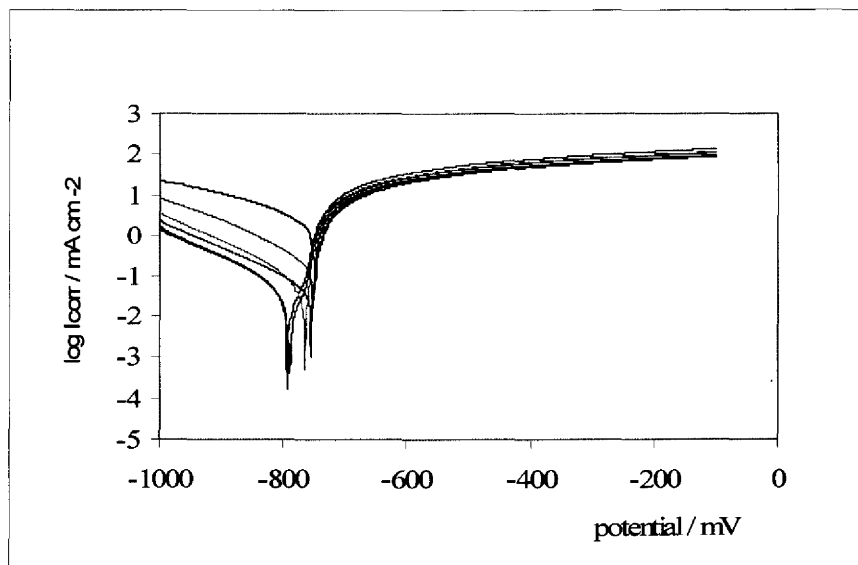
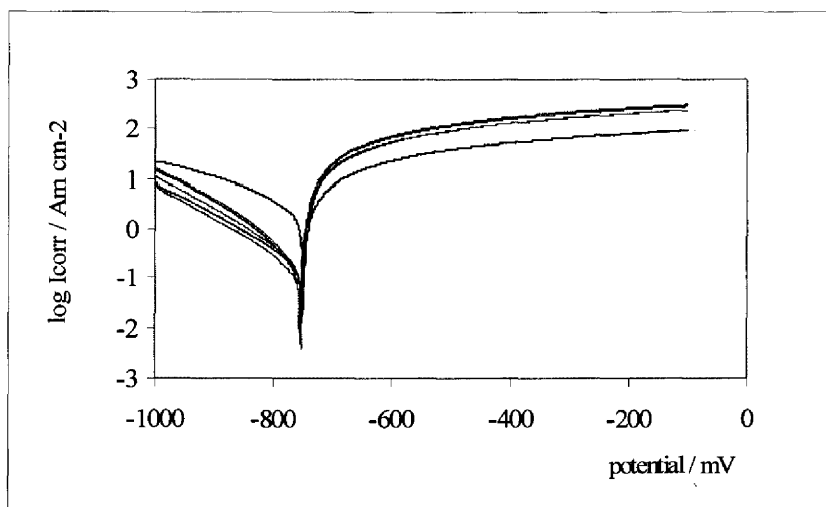


Figure 3: Polarization curves for the aluminium in 0.5M HCl with and without various concentrations of compound 2



Note:  
 Red – 0.1 g L<sup>-1</sup> Blue – 0.2g L<sup>-1</sup> Green – 0.3g L<sup>-1</sup> Pink – 0.4g L<sup>-1</sup>  
 Purple – 0.5 g L<sup>-1</sup> Black - Blank

Figure 4: Polarization curves for the aluminium in 0.5M HCl with and without various concentrations of compound 3



Note:  
Red – 0.1g L<sup>-1</sup> Blue – 0.2g L<sup>-1</sup> Green – 0.3g L<sup>-1</sup>  
Pink – 0.4 g L<sup>-1</sup> Purple – 0.5 g L<sup>-1</sup> Black - Blank

Figure 5: Polarization curves for aluminium in 0.5M HCl with and without various concentrations of compound 4

Table 3: Electrochemical parameters for aluminium in 0.5 M HCl containing various concentrations of inhibitors at 25°C

Inhibitor	$C_{inh}$	Tafel Plot					
		$E_{corr}$ (mV)	$R_p$ (ohm/c $m^2$ )	$I_{corr}$ (mA/cm <sup>2</sup> )	$B_a$ (mV)	$B_c$ (mV)	%IE ( $I_{corr}$ )
-	Blank	-750.6	25.6	0.7947	39.6	-167.7	0
<b>1</b>	$3.0 \times 10^{-3}$	-764.2	269.20	0.0590	20.8	-87.7	92.6
	$6.0 \times 10^{-3}$	-760.8	162.42	0.1911	29.7	-153.7	75.9
	$9.0 \times 10^{-3}$	-720.3	406.24	0.0281	20.3	-231.2	96.5
	$1.2 \times 10^{-2}$	-751.4	43.36	0.5567	29.1	-185.8	29.9
	$1.5 \times 10^{-2}$	-764.2	321.64	0.1130	24.4	-155.7	85.8
<b>2</b>	$3.0 \times 10^{-3}$	-792.9	641.55	12.6764	53.1	-45.5	137.9
	$6.0 \times 10^{-3}$	-791.5	722.27	10.2183	50.6	-42.7	111.1
	$9.0 \times 10^{-3}$	-759.1	108.50	0.2162	26.4	-183.0	2.4
	$1.2 \times 10^{-2}$	-826.4	587.36	17.1962	65.2	-61.6	187.1
	$1.5 \times 10^{-2}$	-876.6	770.25	10.3828	50.0	-47.3	112.9

Table 4: Electrochemical parameters for aluminium in 0.5 M HCl containing various concentrations of inhibitors at 25°C

Inhibitor	C <sub>inh</sub>	Tafel Plot					
		E <sub>corr</sub> (mV)	R <sub>p</sub> (ohm/cm <sup>2</sup> )	I <sub>corr</sub> (mA/cm <sup>2</sup> )	B <sub>a</sub> (mV)	B <sub>c</sub> (mV)	%IE (I <sub>corr</sub> )
-	Blank	-751.6	8.35	3.5737	150.0	-305.3	0
3	2.8 X 10 <sup>-4</sup>	-791.6	649.72	0.0070134	29.4	-28.1	99.80
	5.6 X 10 <sup>-4</sup>	-794.5	511.16	0.0134029	40.2	-41.9	99.62
	8.4 X 10 <sup>-4</sup>	-757.1	63.89	0.1819	22.2	-117.2	94.91
	1.1X 10 <sup>-3</sup>	-771.0	248.75	0.1071	24.0	-151.3	97.00
	1.4 X 10 <sup>-3</sup>	-763.1	252.54	0.0561	20.0	-144.9	98.43
4	2.8 X 10 <sup>-4</sup>	-768.3	98.90	0.2012	21.8	-150.3	94.37
	5.6 X 10 <sup>-4</sup>	-764.0	61.07	0.3606	25.5	-138.3	89.91
	8.4 X 10 <sup>-4</sup>	-761.9	60.51	0.2731	20.8	-144.4	92.36
	1.1X 10 <sup>-3</sup>	-765.2	50.22	0.4301	25.8	-141.1	87.96
	1.4 X 10 <sup>-3</sup>	-761.2	65.31	0.3552	25.3	-181.6	90.06

### Conclusions

Results prove that compounds 1-4 display inhibition of corrosion properties for aluminium in 0.5 M HCl. The inhibition efficiency is seen to increase in the following order, 2>3>1>4. By using weight loss measurements, the percentage inhibition efficiency is seen to increase with increasing additive concentration. Polarization measurements demonstrate the compounds under investigation act as cathodic and mixed inhibitor.

The adsorption of compounds 1-4 is probably occur on aluminium surface. As far as the inhibition process is concerned , it is generally assumed that the adsorption of the inhibitor at the metal /solution interface is the first step in the action mechanism of the inhibitors in acid media. Four types of adsorption may take place in the inhibiting phenomenon involving Schiff bases at the metal/solution interface: (1) electrostatic attraction between charged molecules and the charged metal, (2) interaction of unshared electron pairs in the molecule with the metal, (3) interaction of  $\pi$  electrons with the metal and (4) a combination of the above (Schweinberg et. al., 1988). The difference in protection action can be attributed to the presence of different substituent to azomethine (C=N) group.

### **Acknowledgment**

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### **References**

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