# INHIBITION EFFICIENCY OF SCHIFF BASES CONTAINING PYRIDYL GROUP AS HCL CORROSION INHIBITORS FOR LOW CARBON STEEL

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### Introduction

Some Schiff bases have recently reported as effective corrosion inhibitors for mild steel [1, 2], aluminium alloys [3] in acidic media and as inhibitors for halide corrosion of copper [4, 5].

In the present study the inhibiting effect of some Schiff bases containing nitrogen and/or sulphur heteroaromatic compound as substituents in their structure for the corrosion of low carbon steel in 0.1M HCl solution have been investigated. Effects of concentration and substituents on the inhibition efficiencies of the selected Schiff bases have been studied systematically.

### Experimental

The formula of the examined Schiff bases, synthesised in the laboratory according to published methods [6, 9], are shown in Figure 1. Test solutions were deaerated by bubbling ultra pure oxygen-free nitrogen gas for 60 min before use and continued during the tests.

The tests were performed in a three-compartment electrochemical cell. The reference electrode was silver-silver chloride (Ag|AgCI|CI) electrode and the auxiliary electrode was platinum electrode.

The potentiodynamic polarisation studies and electrochemical impedance (EIS) measurements were performed by using CHI 604 Electrochemical Analyser. Working electrode was first immersed into the test solution for 60 minute to establish a steady state open circuit potential. After measuring the open circuit potential potentiodynamic polarisation curves were obtained with a scan rate of  $0.5 \text{mV.s}^{-1}$  in the potential range from -600 mV to +600 mV relative to the corrosion potential. Corrosion current density values were obtained by Tafel extrapolation method. Electrochemical impedance (EIS) measurements were performed at open circuit potential in the frequency range from 100 kHz – 1 Hz with a signal amplitude perturbation of 5 mV at 20 °C.



2-((1Z)-1aza-2-(2-pyridyl)vinyl)benzene-1-thiol

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[((1Z)-1aza-2-(2-pyridyl)vinyl)amino]benzene-1-thione

PVB



2-((1Z)-1aza-2-(2-pyridyl)vinyl)benzothiazole

Fig. 1 Molecular structure of the investigated Schiff bases

### **Results and discussion**

### Potentiodynamic polarisation and AC impedance results

Figure 2 shows the anodic and cathodic polarisation curve of low carbon steel in 0.1M HCl solution without and with DPE. Similar polarisation curves were obtained in 0.1M HCl solutions with different concentrations of PVBT, PVA and PVB. Electrochemical parameters obtained from the Tafel extrapolation method of the polarisation curves are given in Table 1. It is observe that both the cathodic and anodic curves show a lower

current density in the presence of the DPE, PVBT, PVA and PVB additives than those recorded in HCl solution and increase in concentration of added Schiff bases cause shifting of corrosion potentials to noble direction and variation in both of Tafel slopes. But anodic Tafel slopes are more enhanced so inhibition of corrosion of low carbon steel in 0.1M HCl solution by studied Schiff bases is under anodic control [10].



**Fig. 2** Tafel polarisation curves for low carbon steel in 0.1M HCl solution without (—) and with 5 .  $10^{-4}$  M ( $\nu\nu$ ),5 .  $10^{-5}$ M (HH) and 5 .  $10^{-6}$ M ( $\lambda\lambda$ ) concentrations of DPE

inhibitor	concentration (mol.l <sup>-1</sup> )	E <sub>corr</sub> ( mV )	İ <sub>corr</sub> (μΑ/cm²)	β <sub>a</sub> ( mV )	β <sub>c</sub> ( mV )	% IE	θ
	0.1	-481	1380	141	-197		
	5 . 10⁻ <sup>6</sup>	-443	870	92	-187	36.9	0.369
PVBT	1 . 10 <sup>-5</sup>	-440	537	75	-181	61.0	0.610
	5 . 10 <sup>-5</sup>	-426	186	74	-165	86.5	0.865
	1.10-4	-454	74	86	-172	94.6	0.946
	5 . 10⁻ੰ_	-472	1258	148	-159	8.8	0.088
DPE	1 . 10 <sup>-5</sup> _	-466	891	132	-166	35.4	0.354
	5 . 10 <sup>-5</sup>	-450	794	123	-202	42.4	0.424
	1 . 10 <sup>-4</sup>	-436	758	100	-223	45.0	0.450
	5 . 10 <sup>-6</sup> _	-0.468	1282	134	-180	7.1	0.071
PVA	1 . 10 <sup>-5</sup> _	-0.449	1196	114	-178	13.3	0.133
	5 . 10 <sup>-5</sup>	-0.434	912	104	-244	33.9	0.339
	1 . 10 <sup>-4</sup>	-0.430	851	99	-242	38.3	0.383
	5 . 10 <sup>-6</sup>	-455	1258	122	-167	8.8	0.088
PVB	1 . 10 <sup>-5</sup>	-451	1071	114	-173	22.4	0.224
	5 . 10 <sup>-5</sup>	-436	1018	94	-186	26.2	0.262
	1 . 10 <sup>-4</sup>	-437	914	90	-190	33.7	0.337

**Table 1** Tafel Polarisation parameter values and corresponding inhibition efficiencies for the corrosion of low carbon steel in 0.1M HCl without and with addition of various concentrations of examined Schiff bases at 20°C

Corrosion inhibition behaviour of low carbon steel in 0.1M HCl with different concentrations of studied additives was investigated by AC impedance measurements. Figure 3 shows the impedance diagram for low carbon steel in 0.1M HCl solution without and with various concentrations of DPE. Similar Nyquist diagrams were obtained in 0.1M HCl with PVBT, PVA and PVB. From Figure 3 comparing the impedance behaviour of low carbon steel in HCl solution with and without Schiff base one will find that the corrosion of low carbon steel is obviously inhibited in the presence of additive. The quantitative results of impedance measurements show that the inhibiting efficiencies of the four inhibitors are increased with increasing concentration. This behaviour reveals that the adsorption of Schiff bases on carbon steel.



**Fig. 3** Nyquist plots for low carbon steel in 0.1M HCl solution without (—) and with 5 .  $10^{-4}$  M (v v), 5 .  $10^{-5}$ M ( $\lambda\lambda$ ) and 5x10<sup>-6</sup>M (*HH*) concentrations of DPE

### Factors influencing the inhibiting efficiency

It is evident from Table 1 that all examined Schiff bases are effective corrosion inhibitors in 0.1M HCl solution. Increase in inhibiting efficiencies with the increase of concentrations of studied Schiff bases shows that inhibition actions are due to adsorption on steel surface.

It is generally assumed that the adsorption of inhibitor at the metal/solution interface is the first step in the mechanism of inhibition in acidic media. Four types of adsorption may take place by organic molecules at the metal/solution interface:

- 1. electrostatic attraction between the charged molecules and charged metal
- 2. Interaction of uncharged electron pairs in the molecule with the metal,
- 3. Interaction  $\pi$  electrons with the metal and
- 4. 4.Combination of 1 and 3.

Chemisorption involves the share or transfer of charge from the molecules to the surface to form a coordinate type bond. Electron transfer is typical for transition metals having vacant low-energy orbitals. As for inhibitors, the electron transfer can be expected with compounds having relatively loosely bound electrons [11].

The establishment of isotherms that describe the adsorption behaviour of corrosion inhibitor is an important as they can provide important clues to the nature of metal-inhibitor

interaction. The plot of log[ $\theta$  / (1- $\theta$ )] versus log c shows that the adsorption of studied Schiff bases obeys Langmuir adsorption isotherm From the obtained straight lines in log[ $\theta$  / (1- $\theta$ )] – log c graphs, equilibrium constants for adsorption process , K<sub>ads</sub>, and free energy of adsorption  $\Delta G_{ads}$ , were calculated . Obtained values of free energy of adsorption  $\Delta G_{ads}$ , are negative which reveals the spontaneity of adsorption process and stability of the adsorbed layer on the steel surface[12, 13].

Examination of polarisation data given in Table 1 shows that the inhibiting efficiency values examined Schiff bases follows the order PVBT > DPE > PVA > PVB. Similar order of inhibition efficiency obtained from EIS was observed from the examination of Nyquist diagram for PVBT, DPE, PVA and PVB. The effectiveness of a compound as corrosion inhibitor depends on the structure of the organic compound. The variation in inhibiting efficiency mainly depends on the type and the nature of the substituents present in the inhibitor molecule. The difference in protection actions of studied inhibitors can be attributed to the presence of substituents that increase or decrease electron density of azomethine (– C = N –) group. The difference in inhibiting efficiency between PVBT and DPE arises due to presence of benzen-thiol in PVBT instead of presence of  $\pi$  electron deficient ring (i.e. pyridine). Benzen-thiol increase the electron density on azomethine group as well as –SH group acts as additional adsorption centre.

On the other hand in PVA molecule following tautomeric equilibrium may take place:



So certain fraction of PVA may exist in mercapto tautomeric form. When PVA is as mercapto tautomeric form, electron withdrawn effect of -C = N - double bond decrease electron density of imine group. The least inhibition efficiency of PVB can be explained by considering geometric structure of PVB (Figure 1). From the values of dihedral angles it can be understood that PVB is in transoid structure and due to this structure full conjugation exist in PVB which turns to decrease electron density in imine group.

### Conclusions

- Inhibition efficiencies of Schiff bases depends on the type and the nature of the substituent present in molecule and follows the order PVBT > DPE > PVA > PVB.
- The inhibition efficiencies of Schiff bases increased with increasing of the concentration of inhibitor.
- Studied Schiff bases behave as anodic inhibitor.
- Adsorption of Schiff bases on low carbon steel surface in 0.1M HCl solution was found to obey Langmuir's adsorption isotherm.

## References

- H. Shorky, M. Yuasa, I. Sekine, R.M. Issa, H.Y. El-Baradie, G.K. Gomma: Corros. Sci. 40 (1998) 2173.
- 2. C.D. Bain, E.B. Throughton, Y.T. Tao, J. Evall, G.M. Whiteside, J.G. Nuzzo: J. Am.Soc. **111** (1989) 321.
- 3. R.G. Nuzzo, E.M. Korenic, L.H. Dubois: J. Chem. Phys., 93 (1980) 767.
- 4. Z. Quan, S.H. Chen, Y. Li, X. Cui: Corros. Sci., 44 (2002) 703.
- 5. S.L. Li, Y.G. Wang, S.H. Chen, R. Yu, S.B. Lei, H.Y. Ma, D.X. Liu: Corros. Sci. **41** (1999) 1769.
- 6. B. Erk, A. Dilmac, Y. Baran, A. Balaban: Synth. React. Inorg. Met. Org. Chem. **10** (2000) 30.
- 7. N.I. Dodoff, Ü. Özdemir, N. Karacan, M.C. Georgieva, S.M. Konstantinov, M.E. Stefanova: Z. Naturforch **54B** (1999) 1553.
- 8. F.E. Anderson, C.J. Duca, J.V.Scudi: J. Am. Chem.Soc. 73 (1951) 4967.
- 9. N.K. Jha, D.M. Joshi: Synth. React. Inorg. Met. Org. Chem. 14 (1984) 455.
- 10. T.Vasudevan, B.Muralidharan, S.Muralidharan, S.Venkatakrishnalyer: Anti-Corros. Method M. **45** (1998) 120.
- 11. F.Mansfeld: Corrosion Mechanisms. Marcel Dekker, New York 1987, p.119.
- 12. M. Hosseini, S.F.L. Mertens, M. Ghorbani M.R. Arshadi: Mater. Chem. Phys. **78** (2003) 800.
- 13. Z. Szlarska-Smialowska: Corros. Sci. 18 (1978) 557.