INHIBITION OF CORROSION OF CARBON STEEL IN HCl SOLUTIONS BY VARIOUS SCHIFF BASE

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Introduction

Evaluation of corrosion inhibitors for steel in acidic media is important for some industrial facilities as well as is very interesting from theoretical aspects. Most of the effective inhibitors are organic compounds containing nitrogen, phosphorus and sulphur in their structures [1, 2]. Heteroatoms such as nitrogen, oxygen and sulphur are capable of forming coordinate covalent bond with metal owing to their free electron pairs and thus acting as inhibitor. Compounds with π-bonds also generally exhibit good inhibitive properties due to interaction of π orbital with metal surface. Schiff bases -with $RC = NR'$ as general formula- have the both features combined with their structure which may then give rise to particularly potential inhibitors.

The aim of this work is to investigate inhibitive effect of some Schiff bases containing nitrogen and/or sulphur heteroaromatic compound as substituents in their structure for the corrosion of carbon steel in 0.1M HCl solution. Effects of concentration, temperature and substituents on the inhibition efficiencies of the selected Schiff bases have been studied systematically.
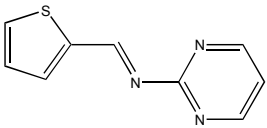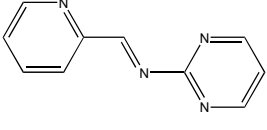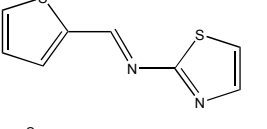
Experimental

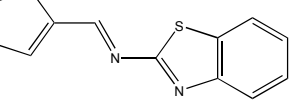The molecular structures of the examined Schiff bases are listed in Table 1. Studied Schiff bases were synthesised according to published methods [3-6]. Solutions were prepared from double distilled water. Test solutions were deaerated by bubbling ultra pure oxygen-free nitrogen gas for 30 min before use and continued during the tests.

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Table 1. *List of investigated schiff bases*

Molecule	Structure	Abbreviation
	2-((1E)-2-aza-2-pyrimidine-2-ylvinyl)thiophene)	PT
	2-((1Z)-1-aza-2-(2-pyridyl)vinyl)pyrimidine)	PP
	2-((1E)-2-aza-2-(1,3-thiazol-2-yl) vinyl) thiophene)	TT
	2-((1Z)-1-aza-2-(2-thienyl) vinyl) benzothiazole)	TBT

The tests were performed in a three-compartment electrochemical cell. The reference electrode was silver-silver chloride (Ag│AgCl│Cl⁻) electrode and the auxiliary electrode was platinum electrode.

Potentiodynamic current – voltage characteristics were measured with EG&G PAR363 model potentiostat, VSG 2000 model voltage scan generator and TQ DMS2 model data management system and measured data were saved by PC386.Working electrode was first immersed into the test solution for 30 min to establish a steady state open circuit potential. After measuring the open circuit potential potentiodynamic polarisation curves were obtained with a scan rate of 0.5mV/s in the potential range from –500mV to +500mV 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 100kHz-1Hz with a signal amplitude perturbation of 5mV by using CHI 604 Electrochemical Analyser at 20^0C.

Results and Discussion

Representative Tafel polarisation curves of carbon steel in 0.1M HCl solutions with different concentrations of PT is shown in Figure 1. Similar polarisation curves were obtained in 0.1M HCl solutions with different concentrations of PP, TT and TBT.
Electrochemical parameters obtained from the Tafel extrapolation method of the polarisation curves are given in Table 2.
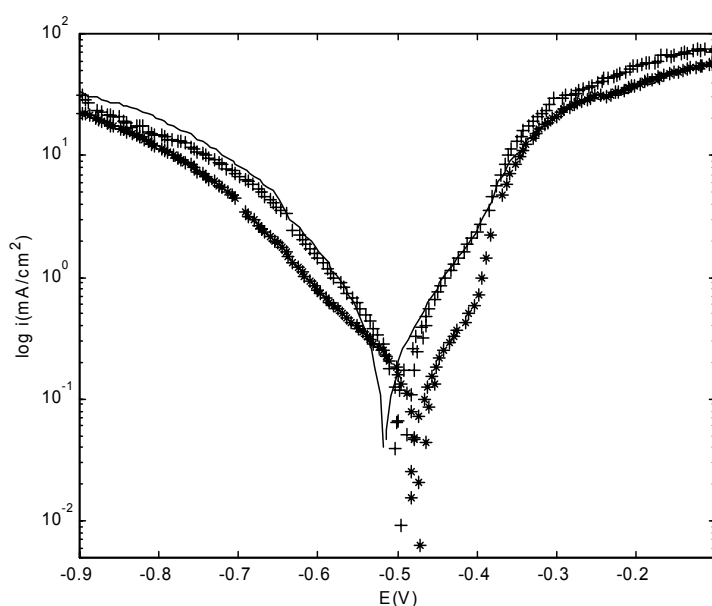
Fig. 1. *Tafel polarisation curves for carbon steel in 0.1M HCl (—) in the presence of 1x10⁻⁴M PT (···) and 1x10⁻⁵M PT (₊₊₊)*

Table 2. *Polarisation parameters and corresponding inhibition efficiencies for the corrosion of carbon steel in 0.1M HCl without and with addition of various concentrations of Schiff bases at 20⁰C*
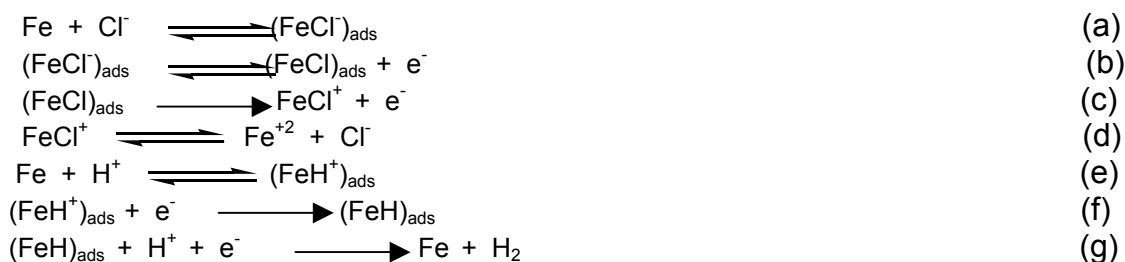
Inhibitor	Concentration (M)	E_{corr} (mV)	β_a (mV)	β_c (mV)	i_{corr} ($\mu A/cm^2$)	IE	θ
—	$1x10^{-1}$	-526	129.2	-127.54	450	—	—
PT	$1x10^{-4}$	-440	40.3	-150.0	75	83.3	0.833
	$5x10^{-5}$	-462	68.4	-141.1	100	77.8	0.778
	$1x10^{-5}$	-486	75.0	-121.5	173	57.4	0.574
	$5x10^{-6}$	-487	80.5	-125.0	213	52.8	0.528
	$1x10^{-6}$	-491	76.9	-123.3	225	50.0	0.500
PP	$1x10^{-4}$	-487	63.8	-140.2	127	71.8	0.718
	$5x10^{-5}$	-502	86.7	-118.9	160	64.4	0.644
	$1x10^{-5}$	-500	84.8	-101.2	189	60.0	0.600
	$5x10^{-6}$	-513	109.8	-122.5	236	47.5	0.475
	$1x10^{-6}$	-510	95.9	-129.0	267	40.7	0.407
TT	$1x10^{-4}$	-490	67.8	-89.1	160	64.4	0.644
	$5x10^{-5}$	-497	80.3	-119.4	211	53.1	0.531
	$1x10^{-5}$	-503	97.0	-126.7	255	43.3	0.433
	$5x10^{-6}$	-513	108.0	-114.6	282	37.3	0.373
	$1x10^{-6}$	-526	116.1	-122.6	367	18.5	0.185
TBT	$1x10^{-4}$	-510	86.9	-125.6	227	49.5	0.495
	$5x10^{-5}$	-513	106.5	-138.2	255	43.4	0.434
	$1x10^{-5}$	-519	94.3	-114.1	289	35.8	0.358
	$5x10^{-6}$	-526	127.0	-134.7	350	22.2	0.222
	$1x10^{-6}$	-516	95.2	-105.8	367	18.4	0.184

Corrosion currents obtained in 0.1M HCl solutions with Schiff bases are lower than corrosion currents obtained in acid solution without Schiff bases. Increase in concentration of added Schiff bases causes 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 carbon steel in 0.1M HCl solution by the studied Schiff bases is under anodic control. Increase in inhibition efficiencies with the increase of concentrations of studied Schiff bases shows that inhibition actions are due to adsorption on steel surface. Four types of adsorption may take place by organic molecules at 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 π electrons with the metal and
4. Combination of 1 and 3 [7].

In hydrochloric acid solution the following mechanism is proposed for the corrosion of iron and steel [8].

$$Fe + Cl^- \rightleftharpoons (FeCl^-)_{ads} \tag{a}$$
$$(FeCl^-)_{ads} \rightleftharpoons (FeCl)_{ads} + e^- \tag{b}$$
$$(FeCl)_{ads} \longrightarrow FeCl^+ + e^- \tag{c}$$
$$FeCl^+ \rightleftharpoons Fe^{+2} + Cl^- \tag{d}$$
$$Fe + H^+ \rightleftharpoons (FeH^+)_{ads} \tag{e}$$
$$(FeH^+)_{ads} + e^- \longrightarrow (FeH)_{ads} \tag{f}$$
$$(FeH)_{ads} + H^+ + e^- \longrightarrow Fe + H_2 \tag{g}$$

In acidic solution imine group as well as nitrogen atoms in heteroaromatic ring can be protonated. Physical adsorption may take place due to electrostatic interaction between protonated forms of Schiff bases and $(FeCl^-)_{ads}$ species. Coordinate covalent bond formation between electron pairs of unprotonated S atoms in heteroaromatic ring and metal surface can take place. Chemisorption of Schiff bases due to interaction of their π orbitals with metal surface occurs following deprotonisation step of the physically adsorbed protonated forms of Schiff bases.

Examination of experimental data shows that the inhibition efficiency values of the examined Schiff bases follows the order PT > PP > TT > TBT. The variation in inhibitive efficiency mainly depends on the type and the nature of the substituents present in the inhibitor molecule. The difference in protection action can be attributed to the presence of different substituents to azomethine ($- C = N -$) group. The difference in inhibition efficiency between PT and PP arises due to presence of π electron excess ring (i.e. thiophene) in PT instead of presence of π electron deficient ring (i.e. pyridine) in PP as substituent. Presence of electron releasing π electron excess ring in PT causes increase of electron density of $-C = N-$ group which gives a better protective action of steel surface than PP. On the other hand difference in inhibition efficiency between PT and TT can be explained by the presence of thiazole ring in TT instead of presence of pyrimidine ring in PT. Chemisorption of studied Schiff bases arise from the interaction of ($- C = N -$) group, π electrons of the aromatic ring and free electron pairs of heteroatoms (S or N) with steel surface. In the case of difference in inhibition efficiencies between PT and TT arise not only in the difference from the electron density of ($- C = N -$) group but from the difference of strength of interaction free electron pairs on N atom in pyrimidine ring and the strength of interaction free electron pairs of N in thiazole ring with metal. Free electron pairs on N atom in pyrimidine ring are more available than free electron pairs on N atom in thiazole ring, because free electron pairs on sulphur participate conjugation in thiazole ring. On the other hand the difference between inhibition efficiencies of TT and TBT arises due to

presence of benzene ring in TBT as a fused to thiazole ring which turns to decrease electron density on S atom in thiazole ring as a result of elongated conjugation.

Since adsorption isotherms can provide important clues to the nature of metal-inhibitor interaction it was established isotherms that describe the adsorptive behaviour of the studied corrosion inhibitor. Several adsorption isotherms were assessed and the Temkin adsorption isotherm was found to provide best description of the adsorption behaviour of the investigated Schiff bases.From the obtained straight lines in θ - lnc graphs, equilibrium constants for adsorption process , K_{ads}, were obtained . The values of free energy of adsorption, ΔG_{ads}, calculated from adsorption isotherms are negative which reveals the spontaneity of adsorption process and stability of the adsorbed layer on the steel surface. The obtained values of the adsorption free energy, ΔG_{ads}, were > -49 kj/mol to   −58 kj/mol are indicative of chemisorption [9].

Corrosion inhibition behaviour of carbon steel in 0.1M HCl solution with different concentrations of the studied Schiff bases and its blank solution was investigated by EIS at 20^0C. Figure 2 shows the impedance diagram for carbon steel in 0.1M HCl solution without and with $1x10^{-4}$M and $1x10^{-6}$M concentrations of PT at 20^0C. Similar Nyquist diagrams were obtained in HCl solution with PP, TT and TBT. R_t values and inhibition efficiencies are increased with increasing concentrations of Schiff bases. This behaviour reveals the adsorption of Schiff bases on carbon steel.
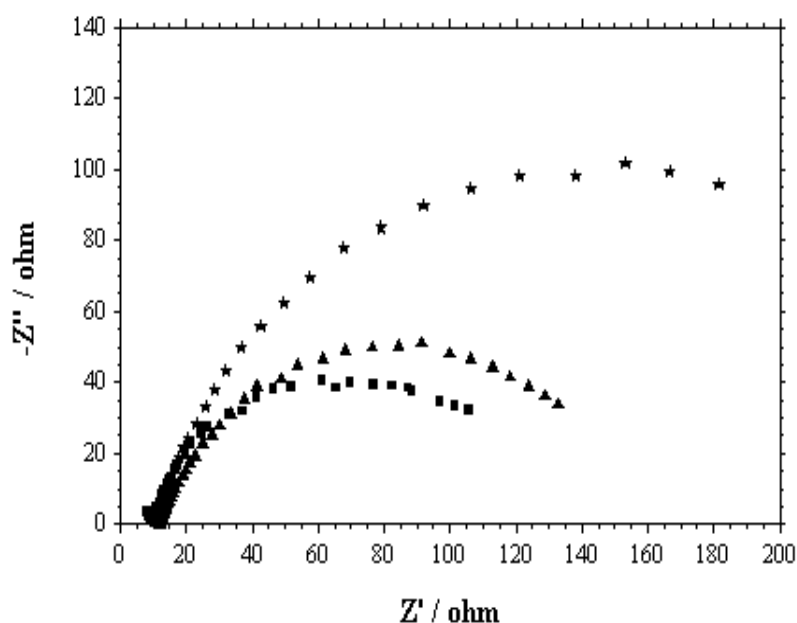

Fig. 2. *Nyquist impedance diagrams for carbon steel in 0.1M HCl (v) solutions containing 1x10⁻⁴M PT ([) ,   1x10⁻⁶M PT(σ)FIG 2*

As mentioned in Tafel polarisation results the effectiveness of studied Schiff bases as corrosion inhibitors depends on the type and nature of the substituents present in the inhibitor molecule. Inhibition efficiencies of the studied Schiff bases obtained from EIS methods are not same as obtained from Tafel extrapolation method given in Table 2, but the trends of their inhibition efficiencies are the same.

Conclusions

- Inhibition of corrosion of carbon steel in 0.1M HCl by the Schiff bases are under anodic control.
- Inhibition efficiencies of Schiff bases depends on the substituent present in inhibitor molecule and follows the order PT > PP > TT > TBT.
- Increasing the charge transfer resistance, Rt values of inhibitor with increase in the concentration of Schiff bases shows that inhibitive abilities of inhibitors depends on the adsorption of molecule on metal surface.
- The adsorption of Schiff bases on carbon steel in 0.1M HCl solution obeys Temkin's adsorption isotherm.

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