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SCHIFF BASES DERIVED FROM ISATIN AS MILD STEEL CORROSION INHIBITORS IN 1 M HCl

(Bes Schiff Yang Terhasil Daripada Isatin Sebagai Perencat Kakisan Keluli Lembut Dalam 1 M Asid Hidroklorik)

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Abstract

Two Schiff bases namely, 3-(phenylimino)indolin-2-one (PII) and 3,3- (1,4-phenylenebis (azan-1-yl-1-ylidene))diindolin-2-one (PDI) were successfully synthesized from the condensation reaction giving yields of 72% and 84%, respectively. The ligands were characterized *via* physical and spectroscopic techniques namely melting point, Elemental Analysis (C, H, N), ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) and Fourier Transform Infrared (FTIR) Spectroscopy. The corrosion inhibiting property of the Schiff bases on mild steel in 1 M HCl solution were investigated by the weight loss measurements, electrochemical impedance spectroscopy (EIS) and linear polarization resistance (LPR). The concentrations of the Schiff bases were varied from 1 x 10^{-3} M to 1 x 10^{-5} M. The inhibition efficiencies obtained from all the methods employed were in good agreement where the percentage of inhibition efficiencies increased with concentration. Results showed that PDI was the better inhibitor with inhibition efficiency of 84% at 1 x 10^{-3} M additive concentration. This is likely due to the effect of its bigger molecular size, higher number of heteroatoms and bigger π-electron cloud of the conjugated double bond system.

Keywords: Schiff base, Isatin, Corrosion inhibitor, Mild steel, Hydrochloric acid

Abstrak

Dua bes Schiff, 3-(phenylimino)indolin-2-one (PII) dan 3,3- (1,4-phenylenebis (azan-1-yl-1-ylidene))diindolin-2-one (PDI) telah disintesis dengan jaya dari reaksi kondensasi memberikan hasil 72% dan 84%. Ligan-ligan telah dicirikan oleh pelbagai teknik kimia-fizikal seperti menentu takat lebur, analisis unsur, ^{1}H and ^{13}C spektroskopi resonans magnet nuklear, dan spektroskopi inframerah. Ciri-ciri perencat kakisan bagi Bes Schiff di atas keluli lembut dalam 1 M asid hidroklorik telah dikaji melalui kaedah penghilangan jisim, spektroskopi impedans elektrokimia dan rintangan polarisasi linear. Kepekatan Bes Schiff disediakan dari 1 x 10^{-3} M to 1 x 10^{-5} M. Kecekapan perencat dari semua kaedah telah menunjukkan keserasian di mana peratus kecekapan perencat meningkat apabila jumlah kepekatan ligan bertambah. Keputusan menunjukkan PDI adalah perencat yang lebih baik dengan kecekapan perencat sebanyak 84% pada kepekatan 1 x 10^{-3} M. Ini adalah kerana efek molekul yang lebih besar, jumlah heteroatom yang tinggi dan π-elektron yang lebih besar dari konjukasi system ikatan kembar.

Kata kunci: Bes Schiff, Isatin, Perencat kakisan, Keluli lembut, Asid Hidroklorik

Introduction

The investigation of corrosion inhibition of mild steel in hydrochloric acid is a subject of practical interest as it is commonly used in many engineering applications [1,2]. The use of organic inhibitors to reduce the corrosion rate of mild steel in acidic medium can be considered to be among the first line of defense against corrosion in the industries [3]. Compounds containing π bonds and lone electron pairs generally exhibit good inhibitive properties as they can facilitate effective adsorption through their interaction with the vacant *d*-orbitals of metal atoms [4,5]. Several studies reported that the inhibition efficiency of a Schiff base was much greater than its precursor molecules due to the presence of -C=N- group(s) in the molecule. Their effectiveness is also related to the chemical composition, molecular structure and their affinities for the metal surface [6,7].

The aim of the present work was to synthesize and characterize two Schiff bases, 3-(phenylimino)indolin-2-one (PII) and 3,3- (1,4-phenylenebis (azan-1-yl-1-ylidene))diindolin-2-one (PDI), to study the corrosion behaviour of mild steel in 1 M HCl using weight loss measurements, linear polarization resistance and electrochemical impedance spectroscopy. Several isotherms were tested for their relevance to describe the adsorption behavior. The differences in inhibitive behavior for the two compounds are explained from their structural properties.

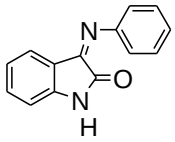
Materials and Methods

Synthesis and characterization of 3-(phenylimino)indolin-2-one, PII

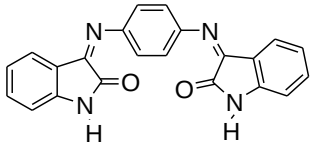
A mixture of 10 mmol of isatin and 10 mmol of aniline in absolute ethanol was refluxed for 6 hours. The precipitate formed was filtered off and washed thoroughly with cold ethanol. The product (Fig. 1) was dried in vacuum pump. Yield = 0.799 g (72%), m.p. 223.7 °C; Found %: C, 74.97; H, 4.54; N, 12.59. Calculated % for $C_{14}H_{10}N_2O$: C, 75.66; H, 4.54; N, 12.60; ν_{max} (KBr): C=N, 1651.8 cm^{-1}; C=C, 1614.57 cm^{-1}; ^{1}H NMR ($CDCl_3$,300MHz) δ/ppm: 6.65-7.44 (9 H, m, Ph), 9.70 (1 H, s, NH), ^{13}C NMR ($CDCl_3$, 75MHz) δ/ppm: 116.1-134.4 (CH Ar), 145.6-150.2 (CN), 154.7 (C=O), 165.4 (C=N).

Synthesis and characterization of 3,3-(1,4-phenylenebis(azan-1-yl-1-ylidene))diindolin-2-one, PDI

A mixture of 10 mmol of isatin and 5 mmol of para-phenylenediamine was synthesized the same manner as PII giving the product as in Fig 1. Yield = 1.53 g, (84%), m.p 328 °C, Found %: C, 72.88; H, 4.14; N, 15.30. Calculated % for $C_{22}H_{14}N_4O_2$ C, 72.12; H, 3.85; N, 15.29 %); ν_{max} (KBr): C=N cm^{-1}, 1649.16; C=C, 1614. 16 cm^{-1}; ^{1}H NMR (DMSO, 300MHz) δ/ppm: 6.67-7.30 (6 H, m, Ph), 2.48 (1 H, s, NH), ^{13}C NMR (DMSO, 75MHz) δ/ppm: 116.2-135.0 (CH Ar), 147.4-147.8 (CN), 155.5 (C=O), 163.9 (C=N).



3-(phenylimino)indolin-2-one (PII)



3,3'-(1,4-phenylenebis(azan-1-yl-1-ylidene)) diindolin-2-one (PDI)

Fig. 1. Molecular structure of the investigated compounds, PII and PDI

Weight loss measurements

Mild steel with the dimension of 1 cm x 1 cm were polished to a mirror finish using 120, 320, 600, 800 and 1200 grit emery paper, immersed in ethanol, washed with deionized water and dried before being weighed. The specimens were immersed for 24 hours in 50 mL 1 M HCl solution containing various concentrations of the inhibitors. The masses before and after immersion were determined using analytical balance. The measurements were done in triplicate, where the average values were used to calculate the inhibition efficiencies.

Electrochemical analysis

Electrochemical experiments were carried out by using a conventional three-electrode cell consisting of a mild steel working electrode, a Ag/AgCl electrode as reference and platinum rod as counter electrode. The working electrode was prepared by embedding the mild steel in epoxy resin and exposing a flat surface of approximately 0.049 cm^2 to the electrolyte. Prior to each measurement, the electrode surface was mechanically abraded with a series of grit emery paper (120, 320, 600, 800, 1200) rinsed with deionized water and dried. The concentrations of the Schiff bases in 1 M HCl were varied from 1 x 10^{-3} M to 1 x 10^{-5} M. In order to obtain a steady state open circuit potential, the working electrode was immersed into the test solution for 15 minutes before the measurements. All experiments were done in triplicate.

Results and Discussion

Synthesis and characterization of PII and PDI

The elemental analysis, ^{1}H NMR and ^{13}C NMR indicated that the desired Schiff bases have been obtained. This was reinforced by the appearance of the characteristic ν(C=N) infrared peaks and the disappearance of ν(C=O) and ν(N-H).

Weight loss measurements

Table 1. Inhibition efficiencies for various concentrations of PII and PDI for corrosion of mild steel in 1 MHCl from weight loss measurements

Inhibitor	Concentration (M)	Weight loss (g)	Inhibition efficiency, η_w (%)
Blank	-	0.0240	-
PII	1×10^{-5}	0.0211	11.9
	1×10^{-4}	0.0133	44.3
	1×10^{-3}	0.0065	72.6
PDI	1×10^{-5}	0.0095	60.4
	1×10^{-4}	0.0067	71.8
	1×10^{-3}	0.0036	85.0

The values of inhibition efficiency obtained from the weight loss method at different concentrations of inhibitors are summarized in Table 1. It is apparent that the inhibition efficiencies increased with inhibitor's concentration. At 1×10^{-3} M concentration for PII and PDI, the inhibition efficiency values obtained are 72% and 85%, respectively. From the measurement, PDI was found to be the more effective inhibitor for mild steel in 1 M HCl.

Impedance measurements

The Nyquist plots of mild steel in 1 M HCl in the presence and absence of PII and PDI are given in Fig. 2 (a) and (b). The impedance parameters are given in Table 2.

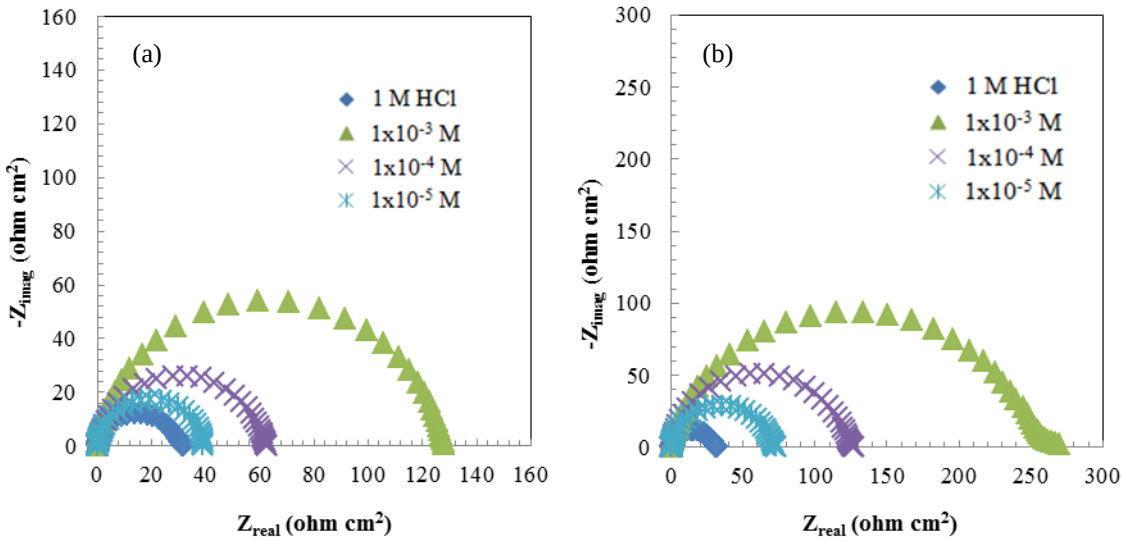


Fig. 2. Nyquist plot for mild steel in 1 M HCl in the presence and absence of different concentrations of (a) PII and (b) PDI.

The impedance response changed with the addition of organic additives. The presence of the two inhibitors enhanced the polarization resistance, R_p, in acidic solution and the effect was more pronounced with PDI that gave a maximum inhibition efficiency of 87.3%. The increase in polarization resistance by increase in inhibitor's concentration indicated the adsorption of inhibitor on metal surface to block the active sites and inhibits corrosion.

Polarization measurements

The Tafel plots of mild steel in 1 M HCl at various concentrations are shown in Fig. 3 (a) and (b), whereas the electrochemical parameters are summarized in Table 3.

From the plots, it can be interpreted that the addition of PII and PDI into the acidic media changed the anodic and cathodic slopes. The changes were more prominent in the anodic domain for PII making it an anodic type inhibitor. This result indicates that the compound was adsorbed on the anodic sites, hence inhibition occurred.

As for PDI, the addition of additive decreased both anodic and cathodic current densities and produced a small shift in the corrosion potential to more noble values. Thus these prominent changes suggested that it is a mixed type inhibitor.

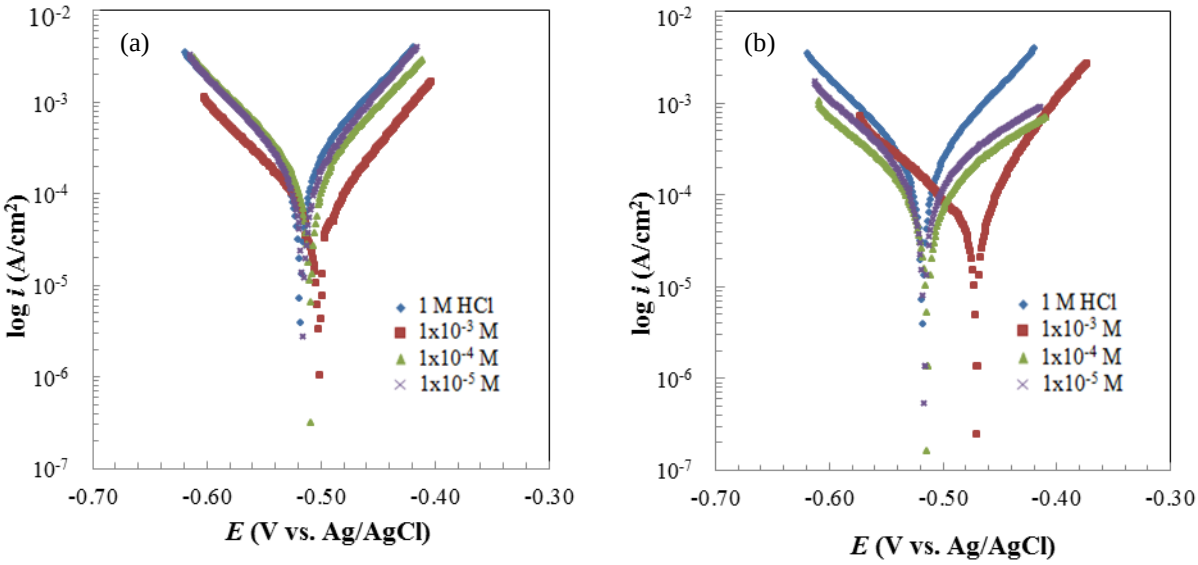


Fig. 3. Tafel plot for mild steel in 1 M HCl in the presence and absence of different concentrations of (a) PII and (b) PDI.

Table 2. Impedance parameters for mild steel electrode in 1 M HCl in the presence of different concentrations of PII and PDI

Compound	Concentration,C (M)	Solution resistance, R_s (Ω cm^2)	Polarization resistance, R_p (Ω cm^2)	Inhibition efficiency (%)
PII	Blank 1 M HCl	0.13	31.90	-
	1 x 10^{-5} M	0.16	38.95	17.9
	1 x 10^{-4} M	0.15	61.98	48.4
	1 x 10^{-3} M	0.18	126.90	74.8
PDI	Blank 1 M HCl	0.13	31.90	-
	1 x 10^{-5} M	0.19	72.60	56.1
	1 x 10^{-4} M	0.17	125.70	74.6
	1 x 10^{-3}M	0.24	250.90	87.3

Table 3. Polarization parameters for mild steel electrode in 1 M HCl in the presence of different concentrations of PII and PDI

Compound	Concentration (M)	β_a (mV/dec)	ß$_c$ (mV/dec)	-E_{corr} (mV)	i_{corr} ($\mu A/cm^2$)	Polarization resistance, R_p (Ω cm^2)	Inhibition efficiency (%)	Surface coverage (θ)
PII	Blank 1 M HCl	83.0	91.1	518.0	235.0	47.9	-	-
	1 x 10^{-5} M	78.5	85.5	520.0	191.0	59.3	19.2	0.23
	1 x 10^{-4} M	65.3	70.3	509.0	143.0	82.5	41.9	0.37
	1 x 10^{-3} M	73.3	86.0	501.0	68.6	215.2	77.7	0.69
PDI	Blank 1 M HCl	83.0	91.1	518.0	235.0	47.9	-	-
	1 x 10^{-5} M	52.8	45.4	516.0	51.0	131.1	63.5	0.62
	1 x 10^{-4} M	59.8	52.5	514.0	45.4	188.3	74.5	0.75
	1 x 10^{-3} M	25.6	38.2	471.0	21.7	238.9	80.0	0.93

Adsorption isotherm

Adsorption isotherm can describe the adsorptive behavior of a corrosion inhibitor where it provides important information on the nature of the metal-inhibitor interaction. Several adsorption isotherms were tested for the description of adsorption behavior of studied compounds and it was found to obey the Langmuir adsorption isotherm. The surface coverage, θ, for various concentrations of the inhibitor was been calculated and the plot of C/θ vs. C yields straight lines as shown in Fig 4. Experimental results are in good agreement with Langmuir adsorption isotherm shown in Equation 1:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \quad (1)$$

where C_{inh} is the inhibitor concentration and K_{ads} is the adsorption equilibrium constant.

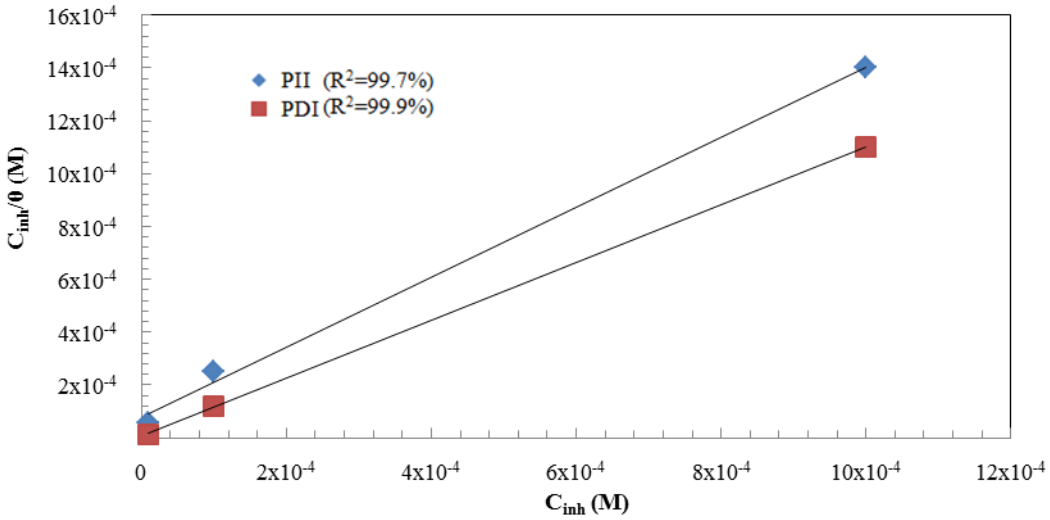


Fig. 4. Langmuir plots for PII and PDI on mild steel in 1 M HCl

The value of K_{ads} is found as 12.5 x 10^3 and 166.7 x 10^3 $M^{-1}$for PII and PDI, respectively. The increasing value of K_{ads} shows increasing adsorption capability of PDI on metal surface [7] due to its structure. The K_{ads} is also related to the standard free energy of adsorption (ΔG_{ads}) according to Equation 2:

$$K_{ads} = \frac{1}{55.5} \exp\left(\frac{-\Delta G_{ads}}{RT}\right) \quad (2)$$

where R is the universal gas constant (J mol^{-1} K^{-1}), T the absolute temperature (K) and 55.5 the value for molar concentration of water in solution (mol L^{-1}).

The values obtained were -33.3 kJ/mol and -39.7 kJ/mol for PII and PDI, respectively. The decreasing value of ΔG_{ads} indicates the increasing adsorption capability and the negative values show spontaneous adsorption of inhibitor molecule on metal surface [4].

The differences in inhibition efficiencies between both compounds are caused by the different sizes of the organic compounds. It is apparent that PDI is larger due to the presence of two of heterocyclic isatin moieties. The introduction of the second π-electron system in PDI gives higher inhibition efficiency value. The inhibition of active dissolution of metal in acidic media is due to the adsorption of inhibitor on metal surface forming protective layers through electron transfer from adsorbed species to vacant orbitals of low energy in metal to form coordinate type link [4]. The more efficient adsorption of PDI compared to PII is attributed to the increase in electron density from the presence of N and O atoms, azomethine groups, heterocyclic and aromatic ring that form effective adsorption on the metal surface.

Conclusion

Both Schiff bases, PII and PDI were successfully synthesized and characterized. Corrosion inhibition investigations showed that both compounds display inhibitor properties. However PDI promoted higher inhibition efficiency because it has a larger size that affected more surface coverage on mild steel and higher electron density that promoted efficient adsorption of the inhibitor on mild steel. The adsorption process obeys the Langmuir adsorption isotherm.

Acknowledgement

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