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Schiff's bases derived from L-lysine and aromatic aldehydes as green corrosion inhibitors for mild steel: Experimental and theoretical studies



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ABSTRACT

Three Schiff's bases (SBs) namely, 2-amino-6 (2-hydroxybenzelideneamino) hexanoic acid (SB-1), 2-amino-6-(4-methoxybenzelideneamino) hexanoic acid (SB-2) and 2-amino-6-((4-dimethylamino)benzylideneamino) hexanoic acid (SB-3) derived from lysine (amino acid) and three different aldehydes were synthesized and evaluated as corrosion inhibitors for mild steel in 1 M HCl solution using weight loss, electrochemical, scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX) and atomic force microscopy methods. The results showed that inhibition efficiency increases with the increasing concentration. Among the studied SBs the SB-3 showed maximum inhibition efficiency of 95.6% at 400 mg L $^{-1}$ concentration. Potentiodynamic polarization study revealed that the investigated SBs act as cathodic type inhibitors. Adsorption of the SBs on mild steel surface obeys the Langmuir adsorption isotherms. The weight loss and electrochemical results were well supported by SEM, EDX and AFM analyses.

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1. Introduction

Mild steel is widely used in several industries as construction material due to its high mechanical properties and low cost [1,2]. However, it is a highly reactive alloy and is very prone to corrosion during many industrial processes including acid cleaning, etching, acid pickling, and acid descaling [3,4]. Among the various available methods of corrosion protection, the consumption of the synthetic corrosion inhibitors is one of the most practical and cost effective method [5,6]. Generally, organic inhibitors inhibit metallic corrosion by adsorbing on the surface and thereby forming a protective barrier between metal and electrolyte (1 M HCl) [7]. The adsorption of these inhibitors on metallic surface are influenced by several factors such as molecular size of inhibitor, nature of substituents, nature of metal and electrolyte [8-10]. Organic compounds containing heteroatoms including nitrogen, sulfur, and/or oxygen with polar functional groups and conjugated double bonds have been reported as effective corrosion inhibitor [11]. The Schiff's bases are important class of compounds characterized by the presence of -CH=N- group. Schiff's bases constitute potential class of corrosion inhibitors and besides this they have many interesting properties and extensive applications in medicinal, agricultural, pharmaceutical fields and material science. Due to the great flexibility and diverse structural aspects, a wide range of Schiff bases have been synthesized and utilized as corrosion inhibitors for metal in aggressive media [12-21]. Most of the available Schiff's base inhibitors are toxic in nature and should be

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replaced by environmental friendly non-toxic inhibitors. Amino acid based Schiff's bases are safe and environmentally benign corrosion inhibitors [22-25]. Previously, some Schiff base compounds have been studied which have shown good inhibition efficiency (70–98%) in the concentration range of 350-2700 ppm [26-28]. In view of above observation it is thought worthwhile to synthesize three Schiff's bases from lysine (amino acid) with three different aldehydes namely, 2-amino-6(2-hydroxybenzelideneamino) hexanoic acid (SB-1), 2-amino-6-(4methoxybenzelideneamino) hexanoic acid (SB-2), 2-amino-6-(4methylamino) benzylideneamino) hexanoic acid (SB-3) to investigate their corrosion inhibition properties on mild steel in 1 M HCl solution. In our case, the best inhibition efficiency (95.6%) was shown by SB-3 at 400 ppm. The choice of these compounds is based on the facts that: (a) they can be synthesized from commercially available cheap and green starting materials, (b) they are likely to show good inhibition efficiency, (c) they have aromatic ring, -CH=N- and hetero-atoms (N, O) through which they can adsorb on the metal surface and inhibit corrosion, and (d) the presence of the -CH=N - group in Schiff bases increases their adsorption ability.

2. Experimental section

2.1. Synthesis of corrosion inhibitor

The SBs used in present study were synthesized according to a method described earlier [29]. The synthetic scheme for SBs is shown in Fig. 1. The purity of the synthesized SBs was determined by thin-layer chromatography using ethyl acetate/n-hexane (4:6) on the silica plate TLC

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Fig. 1. Synthetic rout for investigated SBs.

Table 1IUPAC name, molecular structure, molecular formula, melting point and analytical data of studied SBs.

S. No.	Name of inhibitor	Chemical structure	Analytical data
1	2-Amino-6 (2-hydroxybenzelideneamino) hexanoic acid (SB-1)	OH OH	$\frac{\text{C}_{13}\text{H}_{18}\text{N}_2\text{O}_3 \text{ (mol. wt. 250.29);}}{\text{IR (KBr cm}^{-1}\text{): 3663, 3534, 2848, 2288, 1776, 1733, 1680, 1678, 926, 787, 645; $^{1}\text{H NMR}$} \\ \text{(300 MHz, DMSO)} \delta \text{ (ppm): 1.58, 1.67, 1.74, 3.42, 3.71, 6.87, 7.27, 7.42, 8.88, 9.42}$
2	2-Amino-6-(4-methoxybenzelideneamino) hexanoic acid (SB-2)	N OH	$C_{14}H_{20}N_{2}O_{3}~(mol.~wt.~264.14);~lR~(KBr~cm^{-1}):~3665,~3491,~2854,~2358,~1783,~1635,~1250,~1163,~960,~823,~621;~^1H~NMR~(300~MHz,~DMSO)~\delta~(ppm):~1.25,~1.57,~1.85,~3.58,~3.71,~5.15,~7.41,~7.52,~7.73,~8.57$
3	2-Amino-6-((4-dimethylamino) benzylideneamino) hexanoic acid (SB-3)	, N O O O O O O O O O O O O O O O O O O	$C_{15}H_{23}N_3O_2$ (mol. wt. 277.36); IR (KBr cm $^{-1}$): 3649, 3565, 2818, 2334, 1794, 1741, 1707, 1690, 945, 790, 626; 1H NMR (300 MHz, DMSO) δ (ppm): 1.27, 1.78, 1.93, 3.09, 3.79, 4.54, 5.14, 6.32, 7.54, 8.98

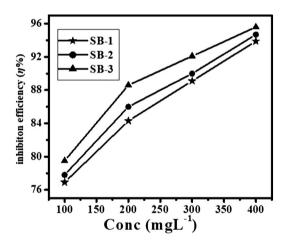


Fig. 2. Variation of inhibition efficiency with SBs concentration.

Table 2The weight loss parameters derived for mild steel in 1 M HCl at different concentrations of SBs.

Inhibitor	Conc (mg L^{-1})	$C_{\rm R} ({\rm mg cm^{-2} h^{-1}})$	Surface coverage (θ)	η%
Blank	0.0	7.66	=	-
SB-1	100	1.76	0.770	77.0
	200	1.20	0.844	84.4
	300	0.83	0.891	89.1
	400	0.46	0.939	93.9
SB-2	100	1.70	0.778	77.8
	200	1.06	0.861	86.1
	300	0.73	0.904	90.4
	400	0.40	0.947	94.7
SB-3	100	1.56	0.796	79.6
	200	0.86	0.887	88.7
	300	0.60	0.921	92.1
	400	0.33	0.956	95.6

Table 3Variation of corrosion rate with temperature in absence and presence of optimum concentration of SBs.

Temperature (K)	Corrosion rate (C_R) (mg cm ⁻² h ⁻¹)				
	Blank	SB-1	SB-2	SB-3	
308	7.60	0.46	0.40	0.33	
318	11.0	2.03	1.90	1.73	
328	14.3	3.40	3.13	2.96	
338	18.6	5.73	5.43	5.23	

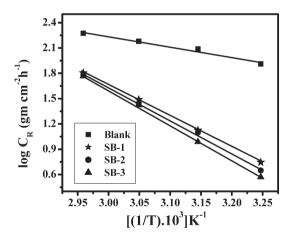


Fig. 3. Arrhenius plots of $\log C_R$ versus 1000/T for mild steel corrosion in 1 M HCl solution in absence and presence of SBs.

Table 4Activation parameters for mild steel dissolution in 1 M HCl in the absence and presence of optimum concentration of SBs.

Inhibitor	E_a (kJ mol ⁻¹)
Blank	28.48
SB-1	70.67
SB-2	74.71
SB-3	80.26

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