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Corrosion resistance properties of Benzhydrylidene-(3, 5-dimethoxy-phenyl)-amine on mild steel in 0. 5M sulphuric acid media

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Abstract

New Schiff base Benzhydrylidene-(3, 5-dimethoxy-phenyl)-amine (BDPA) has been evaluated as effective corrosion inhibitor for mild steel in 0. 5 M H_2SO_4. The inhibition action of the this compound has been investigated by using galvanostatic polarisation. The maximum inhibition efficiency (98. 50%) was observed for 10^{-1} moles/litre BDPA at 25^0C. Polarization studies showed that BDPA acts as a mixed type inhibitor. The influence of inhibitor concentration and immersion time on the corrosion resistance of mild steel has been investigated. The inhibitive action of these compounds is discussed in terms of blocking the electrode surface by adsorption of the inhibitor molecules according to Langmuir isotherm. Thermodynamic parameters (ΔG_{ads}, ΔH_{ads}, ΔS_{ads}) for the adsorption process and kinetic parameters for the metal dissolution (or hydrogen evolution) reaction in the presence of the Schiff base were determined.

1. INTRODUCTION

Mild steel is one of the most commonly used constructional material in various chemical industries owing to its low cost [1], good tensile strength [2] and availability [3]. Also, the uses of acid solutions in chemical industries, such as acid pickling of metals [4], oil well acidification [5], ore production [6] and chemical cleaning and processing are indispensible [7]. Therefore so, the protection of mild steel from acid corrosion is an important topic among the researchers due to its wide range of industrial applications [8]. Several attempts have been made to synthesize various organic and inorganic compounds containing electronegative functional groups (C O, N H, O H and C S) and electron rich aromatic systems [9–12] and investigated as inhibitors for the corrosion of carbon steel[13–15]. Schiff's bases, the condensation

products of aldehydes or ketones with amines, are shown to have excellent corrosion inhibition efficiencies when compared to those of the individual constituents [16–18]. The presence of-C=N-group in Schiff base molecules enhances their adsorption ability and corrosion inhibition efficiency [19, 20]. In addition, the planarity (p) and lone pair of electrons present on the N atoms are the important structural features that determine the adsorption of these molecules to the metal surface [21]. In the present work BDPA was evaluated for its inhibition effect on the corrosion of carbon steel in 0. 5 M H_2SO_4 solutions by electrochemical techniques.

2. Experimental details

2. 1 Materials

The specimens used in this investigation of dimensions 5 cm × 1 cm × 1 cm were prepared from rectangular rod having composition (C = 0. 15%, Si = 0. 08%, S = 0. 025%, P = 0. 025% and Mn = 1. 02%) . These rectangular specimens were fitted by Teflon on a glass tube as a holder, leaving 1 cm^2 of the surface area exposed to the solution. The specimens were mechanically abraded with a series of emery papers up to 1200 grade. Then, it was rinsed in acetone and double-distilled water before immersion in the experimental solution. The corrosive solution was a 0. 5N Sulphuric acid solution diluted from concentrated acid (38%, Merck) with double-distilled water. This solution was used as blank. The inhibitor Benzhydrylidene-(3, 5-dimethoxy-phenyl)-amine was prepared in the concentration range from 10^{-1} to10^{-4}M in blank solution. All tests were performed in deareated solutions under unstirred conditions at 25 °C.

2. 2 Weight loss measurements

Weigh loss (W) experiments were carried out using disc samples of carbon steel having the dimensions 15 mm × 5 mm × 15 mm. Before immersion in the test solutions with or without the inhibitor, the samples were abraded with different SiC paper (220, 500, 800, and 1000) , ultrasonically cleaned in distilled water, rinsed with acetone and finally dried. After 240 h exposure time at room temperature in 100 mL corrosive solutions, the specimens were taken out, brushed under running water to remove the corrosion products, washed with distilled water and acetone and dried. Before and after the corrosive attack the samples have been weighed using an analytical balance (precision ±0. 1 mg) . the surface coverage (θ) and inhibition efficiency (η) of the inhibitor were obtained using Eqs. (1) and (2) :

$$\theta = 1-(W_{corr} / W^{o}_{corr}) \quad (1)$$

$$\eta\ (\%) = \theta \times 100 \quad (2)$$

where W_{corr} and W^{o}_{corr} are the weight loss of the samples in the presence and absence of the inhibitor respectively.

2. 3 Electrochemical measurements.

A three-electrode cell, consisting of carbon steel working electrode (WE) , a platinum counter electrode (CE) , and saturated calomel electrode (SCE) as a reference

electrode, was used for electrochemical measurements. All experiments were performed in atmospheric condition without stirring. Prior to the electrochemical measurement, a stabilization period of 4 hours was allowed, which was proved to be sufficient to attain a stable value of Ecorr. The potentiodynamic polarization curves were recorded in the potential range of −120 to +200 mV (SCE) with a scan rate of 1 mV s−1. All potentials were measured against SCE.

3. Results and Discussion

3. 1 Weight loss measurements

The WL of mild steel specimens after exposure to 0. 5MH_2SO_4 solution with and without addition of various concentrations of BDPA was calculated in gm^{-2} h^{-1} and the data obtained were given in Table 1. It is clear from Table 1 that, the addition of inhibitor to the aggressive solution reduces dissolution rate of mild steel efficiently. The WL was reduced with increasing Schiff base concentration indicates that the inhibitor molecules act by adsorption on the metal surface.

Table. 1. Inhibitor efficiency from weight loss measurement for MS 0. 5M H2SO4 solutions in the presence and absence of inhibitor.

Compound	Concentration (M)	W_{corr} (mg/cm^2h)	η (%)	Q
H_2SO_4	0. 5 M	1. 5151	-	-
BDPA	10^{-4}	0. 8654	42. 88	0. 4288
	10^{-3}	0. 7563	50. 08	0. 5008
	10^{-2}	0. 6746	55. 47	0. 5547
	10^{-1}	0. 5689	62. 45	0. 6245

3. 2 Potentiodynamic polarisation curves:

Fig. 1. Shows the cathodic and anodic polarization curves of mild steel in 0. 5 M H_2SO_4 solutions at 25^0C in the presence of different concentrations of BDPA. It follows tafel behaviour. The corresponding Electrochemical parameters i. e. corrosion potential (E_{corr} versus SCE) , corrosion current density (i_{corr}) and cathodic and anodic tafel slopes (βa, βc) were calculated from these curves and are listed in table 1. Inhibition Efficiency (IE %) was calculated using the relationship (3)

$$\boldsymbol{IE\,\%} = \frac{\boldsymbol{I_{corr} - I_{corr\,(inh)}}}{\boldsymbol{I_{corr}}} \times \mathbf{100} \qquad (3)$$

Where I_{corr} and $I_{corr\,(inh)}$ represent the corrosion current density values without and with inhibitor, respectively.

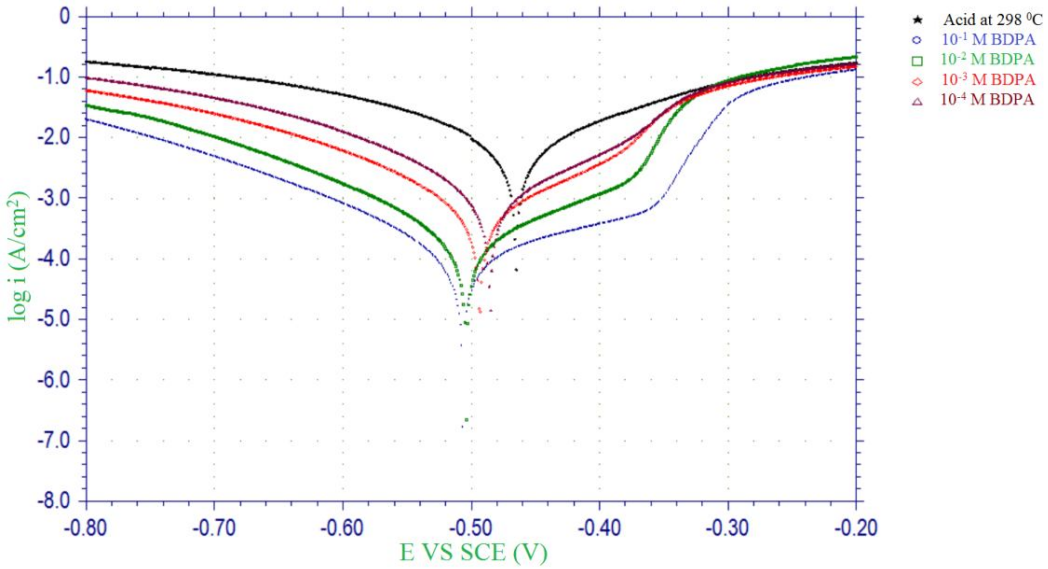

Fig. 1. Tafel polarisation curves for mild steel in 0. 5M H_2SO_4 solution in the presence and in the absence of the BDPA at various concentrations.

The degree of surface coverage (θ) values for different concentrations is calculated by following equation. (4) [22]

$$\theta = 1 - (I_{corr}/I_o) \quad (4)$$

Galvanostatic polarisation studies on mild steel in 0. 5M sulphuric acid solution containing various concentrations reveal that BDPA influences the corrosion parameters (table 2) . This inhibitor has produced a noticeable decrease in the corrosion current density at all the concentrations. The inhibitive action is better expressed by inhibition efficiency which increases with BDPA concentration (Table 2) . The inhibitor efficiency attains the maximum value of 98. 50 % at 10^{-1} M BDPA.

Both anodic and cathodic reactions of mild steel electrode corrosion were inhibited by the increase of concentration of the BDPA. This result suggests that the addition of the BDPA reduces anodic dissolution and also retards the hydrogen evolution reaction [23].

The irregular trends of b_a and b_c values indicates the involvement of more than one type of species adsorbed on the metal surface. Therefore, the adsorption of the π-electron system of BDPA possibly overlaps with the vacant d-orbitals of the surface of iron resulting in a strong dπ–pπ interaction. This electrostatic interaction probably leads to a stronger adsorption of the inhibitor and formation of a barrier between the metal surface and reactive sites. At lower concentration (10^{-4} M) surface coverage drops considerably because of the inability of BDPA to block the active sites, hydrogen permeation onto the metal surface.

There is no remarkable change in the OCP of inhibited solutions from that of uninhibited solution (fig. 1) but there is shift in OCP values towars more negative potential in the presence of higher concentrations of the synthesized inhibitor, suggesting that this compound behave as mixed-type anodic inhibitor.

Table. 2. Electrochemical parameters for the corrosion of mild steel in 0. 5 M H_2SO_4 solution with and without different concentrations of inhibitors at 25 ^{0}C.

Temp	Conc (M)	I_{corr} (mA/cm^2)	-E_{corr} Vs SCE (mV)	b_a (mV/dec)	b_c (mV/dec)	I. E. %	Q
298	Blank	8. 805	465	70. 59	60. 89	-	-
	10^{-4}	0. 894	485	108. 57	84. 69	89. 84	0. 8984
	10^{-3}	0. 699	493	110. 80	85. 17	92. 06	0. 9206
	10^{-2}	0. 364	504	82. 47	90. 47	95. 86	0. 9586
	10^{-1}	0. 131	508	151. 27	90. 89	98. 50	0. 9850

Adsorption isotherm

In the present study, various adsorption isotherms were tested and it was found that the adsorption of Schiff's base on the mild steel surface in acid media follows the Langmuir adsorption isotherm

According to Langmuir's isotherm, surface coverage is related to inhibitor concentration (C) by the following equation [24]

$$C/\theta = 1/ K_{ads} + C \quad (5)$$

where K_{ads} is the equilibrium constant for adsorption process. The plot of C/θ versus C yields a straight line (Fig. 2) with regression coefficient (R^2) close to 1 (0. 9994) suggests that the adsorption of inhibitor molecules follow Langmuir adsorption isotherm. The K_{ads} values can be calculated from line intercept on C/θ axis and is related to standard free energy change of adsorption (ΔG°_{ads}) as follows [25]

$$\Delta G^\circ_{ads} = -2.303RT\log(55.5\, K_{ads}) \quad (6)$$

where R is molar gas constant (8. 314 J mol^{-1} K^{-1}) , T is absolute temperature (K) and value 55. 5 is the concentration of water (in mol dm^{-3}) in the solution.

The calculated ΔG°_{ads} and K_{ads} were listed in Table 3. The negative values of ΔG°_{ads} indicating the spontaneously adsorption of the inhibitor molecules on the metal surface was found to be-20. 39Kj/mol. Values of ΔG°_{ads} around-20 kJ/mol or lower are consistent with the electrostatic interaction between charged organic molecules and the charged metal surface (physisorption) ; those around-40 kJ/mol or higher involve charge sharing or transfer from the organic molecules to the metal surface to form a co-ordinate type of bond (chemisorption) . The values of ΔG°_{ads} for BDPA being less than-40 Kj/mol indicate a physical adsorption. In addition to electrostatic interaction, there may be some other interactions [26].

Table 3. Thermodynamic adsorption parameters for BDPA on mild steel in 1. 0 M H_2SO_4 solution at 298.

Compound	K_{ads}	R^2	$-\Delta G^{\circ}_{ads}$ (kj/mol)
BDPA	67. 56	0. 9994	20. 39

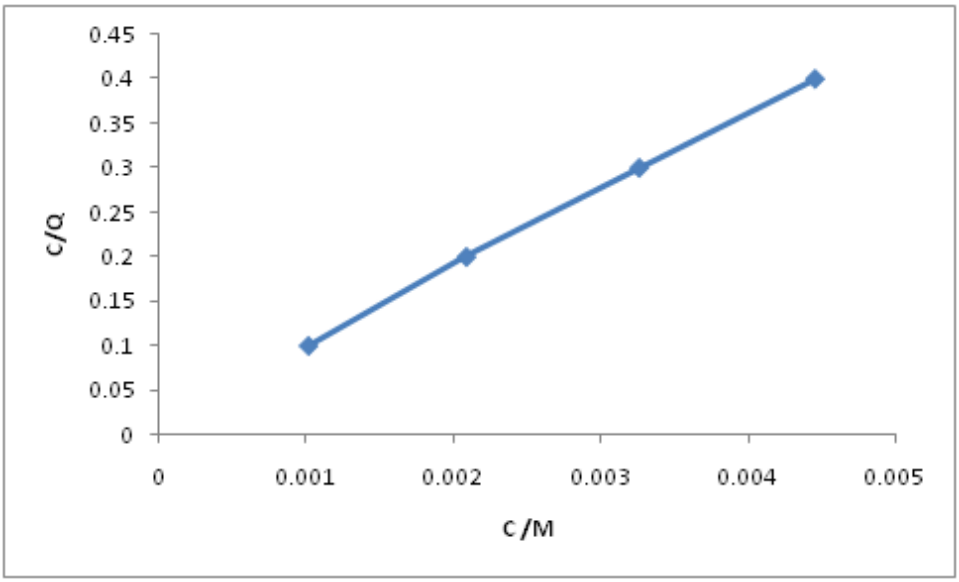

Fig. 2. Langmuir adsorption isotherm of the inhibitor in 1. 0 M H_2SO_4 at 25 ^{0}C:

CONCLUSIONS:

The Schiff base Benzhydrylidene-(3, 5-dimethoxy-phenyl)-amine (BDPA) was Evaluated as possible corrosion inhibitor for mild steel in 0. 5M H_2SO_4 solution.

According to results obtained, the following points can be emphasized:

1. The inhibition efficiency of Schiff base studied depends on its concentration as inhibition efficiency is increasing with increase in concentration of Schiff base. The excellent inhibition efficiency was attributed to the adsorption of inhibitor molecules and protective film formation on the metal surface.
2. The potentiodynamic polarization curves indicated that the BDPA Schiff base inhibits both anodic metal dissolution and also cathodic hydrogen evolution reactions but OCP is becoming more negative with the increase in inhibitor concentration proving it a mix type cathodic inhibitor, with predominantly control of cathodic reaction. .
3. The adsorption of BDPA molecules on the metal surface from 0. 5M H_2SO_4 solution obeys Langmuir adsorption isotherm. The high value of adsorption equilibrium constant and the negative value of standard free energy of adsorption suggested that, the BDPA molecules were strongly adsorbed on mild steel surface and this adsorption took place spontaneously.

4. The standard free energy of adsorption has been found close to −20 kJ mol−1 which indicated that the adsorption is seen more a physical form than chemical adsorption.

REFERENCES:

[1] A. Ostovari, S. M. Hoseinieh, M. Pei Kari, S. R. Shadizadeh, S. J. Hashemi, Corros. Sci. 51 (2009) 1935.
[2] E. E. Oguzie, Mater. Lett. 59 (2005) 1076.
[3] A. Kosari, M. Momeni, R. Parvizi, M. Zakeri, M. H. Moayed, A. Davoodi, H. Eshghi, Corros. Sci. 53 (2011) 3058.
[4] M. A. Amin, S. S. AbdEl-Rehim, E. E. F. El-Sherbini, R. S. Bayoumi, Electrochim. Acta 52 (2007) 3588.
[5] G. Trabanelli, Corrosion 47 (1991) 410.
[6] J. Stjernberg, J. C. Ion, M. L. Antii, L. O. Nordin, B. Lindblom, M. Odenc, J. Eur. Ceram. Soc 32 (2012) 1519.
[7] G. Schmitt, Br. Corros. J. 19 (1984) 165.
[8] K. Emregul, O. Atakol, Mater. Chem. Phys. 82 (2003) 188.
[9] I. M. Issa, M. N. H. Moussa, M. A. A. Ghandour, Corros. Sci. 13 (1973) 791.
[10] A. Popova, E. Sokolova, S. Raicheva, M. Christov, Corros. Sci. 45 (2003) 33.
[11] M. Ozcan, I. Dehri, M. Erbil, Appl. Surf. Sci. 236 (2004) 155.
[12] M. G. Hosseini, S. F. L. Mertens, M. Ghorbani, M. R. Arshadi, Mater. Chem. Phys. 78 (2003) 800.
[13] S. Bilgic, N. Calickan, Appl. Surf. Sci. 152 (1999) 107.
[14] K. C. Emregul, R. Kurtaran, O. Atakol, Corros. Sci. 45 (2003) 2803.
[15] G. K. Gomma, M. H. Wahdan, Mater. Chem. Phys. 39 (1995) 209.
[16] S. Chitra, K. Parameswari, A. Selvaraj, Int. J. Electrochem. Sci. 5 (2010) 1675–1697.
[17] R. Solmaz, Corros. Sci. 52 (2010) 3321–3330.
[18] R. Solmaz, E. A. Sahin, G. Kardas, Mater. Chem. Phys. 125 (2011) 796–801.
[19] K. C. Emregül, O. Atakol, Mater. Chem. Phys. 82 (2003) 188–193.
[20] M. Behpour, S. M. Ghoreishi, M. Salavati-Niasari, B. Ebrahimi, Mater. Chem. Phys. 107 (2008) 153–157.
[21] R. A. Prabhu, T. V. Venkatesha, A. V. Shanbhag, B. M. Praveen, G. M. Kulkarni, R. G. Kalkhambkar, Mater. Chem. Phys. 108 (2008) 283–289.
[22] Niknejad Khomami, M. ; Danaee, I. ; Attar, A. A. ; Peykari, M. Effects of NO2− and NO3 − ions on corrosion of AISI 4130 steel in ethylene glycol + water electrolyte. Trans. Indian Inst. Met. 2012, 65, 303.
[23] K. F. Khaled, N. Hackenman, Electrochim. Acta 49 (2004) 485–495.
[24] E. Machnikova, K. H. Whitmire, N. Hackerman, Electrochim. Acta 53 (2008) 6024.
[25] J. M. Cases, F. Villieras, Langmuir 8 (1992) 1251–1264.
[26] M. Behpour, S. M. Ghoreishi, N. Soltani, M. Salavati-Niasari, M. Hamadanian, A. Gandomi, Corros. Sci. 50 (2008) 2172–2181.