Research Article
Acid Corrosion Inhibition of Steel by Lamotrigine

B. S. Shylesha, T. V. Venkatesha, B. M. Praveen, and S. E. Nataraja

1 Department of Chemistry, School of Chemical Sciences, Kuvempu University, Karnataka 577 451, India
2 Department of Chemistry, Srinivas School of Engineering, Mukka, Mangalore 575 021, India

Correspondence should be addressed to T. V. Venkatesha, drtvenkatesha@yahoo.co.uk

Received 27 August 2012; Accepted 13 September 2012

Academic Editors: G. Bereket, C. Gu, C.-H. Hsu, I. Obot, and E. Stupnisek-Lisac

Copyright © 2012 B. S. Shylesha et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Corrosion inhibition effect of lamotrigine on steel in 1.0 M HCl and 0.5 M H2SO4 was studied by techniques like weight loss, polarisation, and electrochemical impedance spectroscopy. Results indicated that lamotrigine is more competent in HCl than in H2SO4 and is justified by scanning electron micrographs. Protection efficiency increased with the concentration of inhibitor and decreased with temperature. Adsorption study revealed the comprehensive adsorption of lamotrigine molecules on steel surface.

1. Introduction

HCl and H2SO4 acids are widely used in processes like acid pickling, acid cleaning, acid descaling, and oil-well acidizing [1, 2], where the intention is to remove surface scales and deposits keeping the base metal intact. But acids, after the removal of scales and deposits, invariably attack the precious metal leading to deleterious consequences of acid corrosion. Use of inhibitors is the most practical method to combat this. Inhibitors are organic molecules which possess π-electrons, hetero atoms like nitrogen, sulphur, and oxygen [3, 4]. These inhibitors generally act by adsorbing on the metal surface forming a thin protective film. In acid media, electron-rich center gets protonated to become cation, electrostatically binds to cathodic sites of metal thereby hinders cathodic reaction. Electron-rich spots of unprotonated molecule finds anodic reactive sites thus reduce anodic reaction. Thus, a heterocyclic organic molecule comprehensively acts. Recently, considerable amount of effort has been devoted to develop novel and efficient corrosion inhibitors. It is found that molecules containing both N and S can claim excellent inhibition compared with those containing only N or S [5, 6]. bis thiadiazole derivatives [7], thiosemicarbazide derivatives [8], Benzimidazole derivatives [9], and purines [10] have been verified to be efficient inhibitors for steel.

Generally acid pickling is carried out at high temperature [11, 12]. In that case efficiency of the inhibitor generally goes down. Hence, it is important to find inhibitor which is fair at elevated temperatures. The study by Tang et al. [13], Singh and Quraishi [7] showed that thiadiazoles retain inhibition efficiency up to 45°C, bis-thiadiazoles up to 65°C, respectively, and was attributed to chemisorption of inhibitor molecule on steel surface. Oguzie et al. argue that inhibitors containing sulphur heteroatom favor chemisorption whereas nitrogen favour physisorption, on the surface of steel, in acidic media [14].

This made us choose lamotrigine which has potential characters to perform well at elevated temperature. It has five nitrogen, two chlorine atoms, and two aromatic rings. These heteroatoms and π electrons could be active centres for adsorption [15]. Lamotrigine being a small molecule, ease electronic interactions of inhibitor molecule with steel and impede steric effects [16, 17]. Moreover, lamotrigine has a fairly planar in-structure which facilitates it's adsorption on the metal surface [18, 19].

Present study was intended to ascertain the ability of lamotrigine to protect steel at different temperatures in HCl and H2SO4. Further to check the concordance in results by weight loss, Tafel and EIS techniques. Adsorption and thermodynamic factors were to be assessed to establish mechanism of adsorption. Scanning electron microscopic (SEM) images were to be referred to confirm the findings.

2. Experimental

2.1. Materials. Steel coupons having compositions 0.04% C, 0.35% Mn, 0.022% P, 0.036% S, and the rest being Fe
(99.55%) were used for all experiments. Coupons of dimension 4 cm × 2.5 cm × 0.05 cm were used for mass loss method and coupons with an exposed area of 1 cm² (rest is covered with araldite resin) with 2.5 cm long stem were used for polarization and EIS methods. All coupons were abraded by using emery papers (grade no.: 220, 400, 600, 800, and 1200), washed thoroughly with distilled water, degreased with acetone, and dried at room temperature. The corrosive media 1.0 M HCl solutions were prepared using AR grade HCl and double distilled water.

Lamotrigine, also known as Lamictal (IUPAC name: 6-(2,3-dichlorophenyl)-1,2,4-triazine-3,5-diamine), is an anticonvulsant drug used in the treatment of epilepsy and bipolar disorder. It is also used as an adjunct in treating depression, though this is considered off-label usage [20]. The structures of lamotrigine are presented in Figure 1.

2.2. Methods

2.2.1. Weight Loss Measurements. Weight loss measurements were performed by immersing steel specimen in glass beaker containing 100 cm³ of corrosive media (1.0 M HCl and 0.5 M H₂SO₄) without and with different concentrations of inhibitor. After an immersion period of 4 h, specimen was taken out and washed well with distilled water, dried, weighed accurately using digital balance (accuracy: ±0.1 mg, model no.: AA-2200, manufactured by Anamed Instruments Pvt. Limited, MIDC, Navi Mumbai 400706, India). To assess the effect of temperature on the inhibition efficiency of lamotrigine, experiments were carried out at 30, 40, 50, and 60 °C. A digital thermostat (±0.5 °C accuracy) was used for maintaining temperature. All corrosion experiments were carried out in aerated as well as static condition. Each measurement was repeated thrice for reproducibility, and an average value was reported.

2.2.2. Electrochemical Measurements. The electrochemical measurements were carried out in CHI 660C electrochemical analyzer (manufactured by CH Instruments, Austin, USA) at 30 °C. The cell consists of three electrodes, namely, the working electrode (steel), counter electrode (platinum), and reference electrode (SCE). An immersion time of 30 minutes was given to allow the stabilization of the open circuit potential (OCP) potential. Each experiment was repeated for three times and an average value was reported. All reported potentials were with respect to SCE. For Tafel measurements, potential-current curves were scanned from −0.2 V to +0.2 V with respect to open circuit potential (OCP) at a constant sweep rate of 0.01 V sec⁻¹. Corrosion parameters such as corrosion potential (Ecorr), corrosion current (Icorr), cathodic Tafel slope (βc), and anodic Tafel slope (βa) were calculated from the software installed in the instrument.

Impedance measurements were carried out by using AC signal with amplitude of 5 mV at OCP in the frequency range of 100 KHz to 10 mHz. The impedance data were fitted to most appropriate equivalent circuit by using ZSimp Win 3.21 software. The impedance parameters were obtained from Nyquist plots.

2.2.3. Surface Morphology Studies. Scanning electron micrographs of steel surface immersed in 1.0 M HCl and 0.5 M H₂SO₄ containing 2.5 mM lamotrigine, at 30 °C, were taken using scanning electron microscope (JEOL, JSM 6400).

3. Results and Discussion

3.1. Mass Loss Studies. The values of percentage protection efficiency (%ηw) obtained from weight loss experiment for the corrosion of steel in 1.0 M HCl and 0.5 M H₂SO₄ in presence of different concentration of lamotrigine are given in Table 1. The %ηw was calculated from the following relationship:

\[
%\eta_w = \frac{W^w - W}{W^w} \times 100, \tag{1}
\]

where \(W^w\) and \(W\) are weight loss of steel in absence and presence of inhibitor.

3.1.1. Effect of Inhibitor Concentration. The variation of %ηw with concentration of lamotrigine, at 30 °C is shown in Figure 2. It is evident from figure that lamotrigine has remarkable protection ability, both in HCl and H₂SO₄ media. It showed appreciable raise in %ηw with concentration upto 2.5 mM for both HCl and H₂SO₄, thereafter, a marginal rise. At any selected temperature, in HCl or in

![Figure 1](image-url)
Table 2: Polarisation and impedance parameters for steel in 1.0 M HCl and 0.5 M H₂SO₄ in presence of different concentration of lamotrigine.

<table>
<thead>
<tr>
<th>Corrosive media</th>
<th>Inhibitor concentration (mM)</th>
<th>$E_{corr}$ versus SCE (mV)</th>
<th>$I_{corr}$ (μA cm⁻²)</th>
<th>$\beta_c$ (mV dec⁻¹)</th>
<th>$\beta_a$ (mV dec⁻¹)</th>
<th>$%\eta_o$</th>
<th>$R_p$ (Ω cm²)</th>
<th>$C_{dl}$ (μF cm⁻²)</th>
<th>$%\eta_z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>Blank</td>
<td>-0.484</td>
<td>170.0</td>
<td>126</td>
<td>86</td>
<td>—</td>
<td>112</td>
<td>62</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>-0.460</td>
<td>43.2</td>
<td>112</td>
<td>76</td>
<td>74.5</td>
<td>418</td>
<td>27</td>
<td>73.2</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>-0.469</td>
<td>11.4</td>
<td>102</td>
<td>151</td>
<td>93.2</td>
<td>1670</td>
<td>12</td>
<td>93.1</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>-0.467</td>
<td>7.0</td>
<td>112</td>
<td>142</td>
<td>95.8</td>
<td>2941</td>
<td>8.8</td>
<td>96.2</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>-0.460</td>
<td>5.1</td>
<td>112</td>
<td>107</td>
<td>97.0</td>
<td>3350</td>
<td>9.9</td>
<td>96.6</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>Blank</td>
<td>-0.489</td>
<td>155.6</td>
<td>123</td>
<td>88</td>
<td>—</td>
<td>72</td>
<td>71</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>-0.480</td>
<td>49.2</td>
<td>115</td>
<td>77</td>
<td>68.3</td>
<td>222</td>
<td>56</td>
<td>67.5</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>-0.478</td>
<td>30.4</td>
<td>94</td>
<td>65</td>
<td>80.4</td>
<td>590</td>
<td>22</td>
<td>87.5</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>-0.459</td>
<td>20.3</td>
<td>114</td>
<td>134</td>
<td>86.9</td>
<td>1112</td>
<td>16</td>
<td>93.5</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>-0.463</td>
<td>9.8</td>
<td>110</td>
<td>116</td>
<td>93.7</td>
<td>1602</td>
<td>10</td>
<td>95.5</td>
</tr>
</tbody>
</table>

H₂SO₄, $\%\eta_w$ increased with inhibitor concentration which suggests magnitude of adsorption and surface coverage by inhibitor increases with concentration of inhibitor [21].

3.1.2. Effect of Temperature. Variation of $\%\eta_w$ with temperature is shown in Figure 3 which indicated that $\%\eta_w$, for both acids, decreased with the increase of temperature. This suggests desorption of previously adsorbed inhibitor molecules, from the steel surface, at elevated temperature indicating physical adsorption of inhibitor molecules [22, 23]. At any temperature, $\%\eta_w$ stands in the order HCl > H₂SO₄.

3.2. Polarization Studies. The polarization behavior of steel immersed in 1.0 M HCl and 0.5 M H₂SO₄ at 30°C in absence and presence of different concentration of lamotrigine is shown in Figure 4. Electrochemical parameters like corrosion potential ($E_{corr}$), corrosion current density ($I_{corr}$), cathodic Tafel slope ($\beta_c$), anodic Tafel slope ($\beta_a$), and percentage inhibition efficiency according to polarisation studies ($\%\eta_p$) are listed in Table 2. The $\%\eta_p$ was calculated from following relation:

$$\%\eta_p = \frac{I_{corr}^o - I_{corr}}{I_{corr}^o} \times 100,$$

where $I_{corr}^o$ and $I_{corr}$ are corrosion current densities in absence and presence of inhibitor, respectively. Results mainly point out the following: (a) $I_{corr}$ decreased with increase in concentration of inhibitor in the order HCl < H₂SO₄ which reiterates lamotrigine is more effictual in HCl. (b) $E_{corr}$ value was shifted towards less negative (noble) potential. It has been reported that [24] a compound can be classified as an anodic or a cathodic-type inhibitor on the basis of shift in $E_{corr}$ value. If displacement in $E_{corr}$ is greater than 85 mV, towards anode or cathode with reference to blank, then an inhibitor is categorized as either anodic or cathodic type inhibitor. Otherwise inhibitor is treated as mixed type. In our study, maximum displacement in $E_{corr}$ value was around 65 mV indicating lamotrigine is a mixed type inhibitor, in both acids. (c) $\beta_c$ and $\beta_a$ values have changed with respect to inhibitor free solution, for both acids which reiterate that lamotrigine is mixed type inhibitor. Obtained $\%\eta_p$ values are in agreement with $\%\eta_w$ values.

3.3. EIS Studies. Electrochemical impedance spectra for steel in 1.0 M HCl and 0.5 M H₂SO₄ without and with different concentration of lamotrigine inhibitor at 30°C are presented as Nyquist plot in Figure 5. The diameter of semicircle increased with inhibitor concentration and is significant in HCl, reflects the effectiveness of inhibitor [25]. An equivalent
circuit model was proposed to fit and analyze EIS data (Figure 6) [10]. EIS parameters calculated in accordance with equivalent circuit are listed in Table 2. Popova et al. [26] said that sum of charge transfer resistance ($R_{ct}$) and adsorption resistance ($R_{ad}$) is equivalent to polarisation resistance ($R_p$). Inhibition efficiency ($\% \eta_z$) was calculated using following equation:

$$\% \eta_z = \frac{R_p - R_p^e}{R_p} \times 100,$$  \hspace{1cm} (3)

where $R_p$ and $R_p^e$ are polarisation resistance values in presence and absence of inhibitor. Table 2 revealed that $R_p$ values increased and capacitance values decreased with inhibitor concentration for both the acids. Decrease in capacitance, which can result from a decrease in local dielectric constant and/or an increase in the thickness of electrical double layer, suggests that the inhibitor molecules act by adsorption at metal/solution interface [27]. This indicated the formation of a surface film on steel. Obtained $\% \eta_z$ are in good agreement with $\% \eta_p$ and $\% \eta_w$. 

Figure 3: Variation of $\% \eta_w$ with temperature for steel in 1.0 M HCl and 0.5 M H$_2$SO$_4$ in presence of different concentration of inhibitor.

Figure 4: Tafel plots for steel in 1.0 M HCl and 0.5 M H$_2$SO$_4$ containing different concentration of Lamotrigine, at 30°C.
3.4. Surface Morphology Study. SEM images were referred to check the protection of steel surface by inhibitor. SEM images of steel plate immersed in 1.0 M HCl and 0.5 M H₂SO₄ in absence and presence of 2.5 mM concentration of lamotrigine, at 30°C, are given in Figure 7. SEM image of steel in 1.0 M HCl or 0.5 M H₂SO₄ exhibit rough surface with innumerable number of pits, voids, and channels and has an etched surface of various indentation depths. These are essentially due to washing away of soluble corrosion products from metal surface. Whitish/gray spots seen at few locations are corrosion products. SEM image of steel in H₂SO₄ protected from lamotrigine shows better surface conditions with few imperfections of smaller depth with no white spots. SEM image of steel in HCl protected from lamotrigine was least corroded and has retained smooth and glassy surface. Better surface conditions stands in the order HCl > H₂SO₄.

3.5. Adsorption Isotherm. Adsorption isotherms give enough information about the interaction of inhibitor molecules with steel. Surface coverage (θ) defined as %η_w/100 (Table 1) was tested by fitting to various adsorption isotherms like Langmuir, Temkin, Freundlich and Flory-Huggins. However, the best fit was obtained with Langmuir isotherm. According to Langmuir’s isotherm, surface coverage is related to inhibitor concentration (C) by the following equation [28]:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C,$$

where $K_{ads}$ is equilibrium constant for adsorption process. The plot of $C/\theta$ versus $C$ yields a straight line (shown in Figure 8) with regression coefficient close to 1 suggests that adsorption obeys Langmuir isotherm. The $K_{ads}$ values can be calculated from line intercept on $C/\theta$ axis and is related to standard free energy change of adsorption ($\Delta G_{ads}$) as follows [29]:

$$\Delta G_{ads}^{o} = -2.30 R T \log(55.5 K_{ads}),$$

where $R$ is molar gas constant (8.314 J K⁻¹ mol⁻¹), $T$ is absolute temperature (K), and value 55.5 is concentration of water in mol dm⁻³ in solution. Obtained $K_{ads}$ and $\Delta G_{ads}^{o}$ values are listed in Table 3. The negative $\Delta G_{ads}^{o}$ and high $K_{ads}$ value ensures spontaneity of adsorption, stability of the adsorbed film and hence better inhibition efficiency [30]. In our study, negative $\Delta G_{ads}^{o}$ and high $K_{ads}$ values stood in the order HCl > H₂SO₄, meaning Ziprasidone is more efficient in HCl. $\Delta G_{ads}^{o}$ value of −20 kJ mol⁻¹ or lower indicates electrostatic interaction (physisorption), while those around −40 kJ mol⁻¹ or higher are generally accepted to form a coordinate type of bond (chemisorption) [31]. In our study, value of $\Delta G_{ads}^{o}$ is around −33 kJ mol⁻¹, for both HCl and H₂SO₄, which is an intermediate, indicates that adsorption involves mixture of physisorption and chemisorption.
Figure 7: SEM visuals of steel in 1.0 M HCl and 0.5 M H₂SO₄ in absence and presence of 2.5 mM lamotrigine. (a) Absence of inhibitor in 1.0 M HCl, (b) 0.5 M H₂SO₄, (c) 2.5 mM lamotrigine in HCl, and (d) 2.5 mM lamotrigine in H₂SO₄.

Figure 8: Langmuir isotherm for the adsorption of lamotrigine on steel in 1.0 M HCl and 0.5 M H₂SO₄.
<table>
<thead>
<tr>
<th>Corrosive media</th>
<th>Temperature (°C)</th>
<th>$K_{ads} \times 10^3$</th>
<th>$\Delta G_{ads}^{\circ}$ (k mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>30</td>
<td>9.8</td>
<td>−33.2</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>6.2</td>
<td>−32.9</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>2.3</td>
<td>−31.6</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>1.4</td>
<td>−31.2</td>
</tr>
<tr>
<td>H$_2$SO$_4$</td>
<td>30</td>
<td>6.4</td>
<td>−32.1</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>3.6</td>
<td>−31.7</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>2.3</td>
<td>−31.5</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>1.1</td>
<td>−30.7</td>
</tr>
</tbody>
</table>

4. Conclusion

(i) Lamotrigine is an effective inhibitor both in HCl and H$_2$SO$_4$ but stands slightly better in HCl. This was explicitly supported by all methods employed in the present study.

(ii) Inhibition efficiency increased with concentration and decreased with temperature

(iii) Lamotrigine is a mixed type inhibitor.

(iv) Adsorption and thermodynamic study showed mixture of chemisorption and physisorption of inhibitor.

Acknowledgments

The authors are grateful to the authorities of Department of Chemistry, Kuvempu University, Karnataka, India for providing lab facilities. The authors also thank Department of Science and Technology, Government of India, New Delhi, (DST: Project Sanction no. 100/IFD/1924/2008-2009 dated 2.07.2008) for providing instrumental facilities.

References


Submit your manuscripts at http://www.hindawi.com