Inhibition of corrosion of mild steel in 1 N HCl solutions by Schiff base derived from non-traditional oils

S D Toliwal,* Kalpesh Jadav & Tejas Pavagadhi

Department of Industrial Chemistry, Institute of Science and Technology for Advanced Studies and Research (ISTAR), Vallabh Vidyanagar 388 120, India

Received 20 April 2010; accepted 14 July 2011

2-alkyl-N-benzylidenehydrazinecarbothioamide of fatty acid hydrazides from nontraditional oils (neem, rice bran and karanja) have been synthesized and evaluated as corrosion inhibitors for mild steel (MS) in hydrochloric acid (HCl) solution by weight loss method. Adsorption of all Schiff bases on MS surface in acid solution obeyed Temkin’s adsorption isotherm. Inhibition efficiency of these compounds increases with increase in concentration of the compound, and vary with solution temperature, immersion time and concentration of acid solution. Various thermodynamic parameters are also calculated to investigate the mechanism of corrosion inhibition.

Keywords: Corrosion inhibition, Mild steel, Nontraditional oils, 2-alkyl-N-benzylidenehydrazinecarbothioamide

Hydrazides are important starting materials for a wide range of derivatives used as pharmaceutical products, corrosion inhibitors (CIs) and surfactants. Some Schiff bases have recently been reported as effective CIs for mild steel in acidic media and as inhibitors for halide corrosion of copper. Mild steel (MS) is extensively used as fabrication material in sugar, petrochemical, food, paper and textile industries. Therefore, study of CI of MS in acid medium is a subject of pronounced technological significance. Organic compounds are widely used in various industries as CIs in acidic environments. 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 \( \pi \)-bonds also generally exhibit good inhibitive properties due to interaction of \( \pi \) orbital with metal surface. Schiff bases with \( RC = NR' \) as general formula have both the features combined with their structure which may then give rise to particularly potential inhibitors. Acid inhibitors find wide application in industrial field as a component in pretreatment composition, in cleaning solution for industrial equipments and in acidization of oil wells. 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 MS in 1N HCl solution. Effects of concentration, temperature, immersion time and thermodynamic parameters on the inhibition efficiencies of the selected Schiff bases have been studied systematically.

Upgradation and utilization of non-traditional oils has been the subject of various investigative studies. Also, studies have been carried out on development of oleo chemicals as acid CIs.

This study presents CI behaviour of neem oil 2-alkyl-N-benzylidenehydrazinecarbothioamide (BN\(_1\)), rice bran oil 2-alkyl-N-benzylidenehydrazinecarbothioamide (BR\(_1\)), karanja oil 2-alkyl-N-benzylidenehydrazine carbothioamide (BK\(_1\)), on corrosion of MS in HCl solutions.

Experimental Procedure

Materials

Oils were procured from Mahavir oil industries Ltd, Mahemdavad. Physico-chemical analysis of neem, rice bran and karanja by standard BIS methods gave, respectively: sp.gr\(^{25^\circ C}\), 0.917, 0.918 and 0.921; acid value, 15.41, 14.12 and 17.34; iodine value, 75.01, 109.42 and 90.78; refractive index at \( 25^\circ C \), 1.465, 1.462 and 1.458; and saponification value, 188.16, 185.62 and 189.71. Fatty acid composition of oils (Table 1) was determined by gas liquid chromatography (GLC) of methyl esters using capillary column (2 m x 0.32 mm) packed with 50%
cynopropyl phenyl polysiloxane (BP225) at 220°C with nitrogen as carrier gas at flow rate 10 mL/min using FID at an injector temperature of 250°C. All other chemicals were of laboratory grade and were used without any modification.

MS coupons having composition in wt% (C, 0.084; Mn, 0.34; Si, 0.13; P, 0.037; S, 0.095 and remainder iron) with a hole (dia 3 mm) near upper edge have been used for corrosion inhibition study.

Methods

Preparation of methyl ester from oil

Methyl ester from oils were prepared by acid catalyzed esterification method in which 100 g oil was taken in 500 mL round bottom flask and 300 mL methanol and 1 mL concentrated sulfuric acid were added. The contents were refluxed for 4 h on water bath. At the end of reaction, the excess methanol was distilled off and 50 mL distilled water was added. The contents were then transferred to separating funnel and lower aqueous layer was withdrawn. The upper organic layer was washed 2-3 times with 1% sodium carbonate solution to remove un-esterified fatty acids. The esters were purified by distillation under 4-5 mm Hg pressure.

Preparation of fatty acid hydrazides

To a solution of fatty acid esters (0.1 M) in ethanol (150 mL) hydrazine hydrate (95%, 0.2 M) was added. The reaction mixture was refluxed for 3-4 h. It was cooled, and the solid separated was collected, washed and recrystallised from ethanol.

Preparation of Schiff base of fatty hydrazides

Thiosemicarbazide

To a solution of a fatty acid hydrazide (0.02 M) in methanol (50 mL) a solution of potassium thiocyanate (0.03 M) and hydrochloric acid 3 mL was added with constant stirring. The mixture was immediately evaporated to dryness on a steam bath and heated for an additional hour with another 50 mL ethanol. The resulting solid was treated with water, and with little ethanol and recrystallised from ethanol.

Schiff base – A thiosemicarbazides (0.02 M) was added to a solution of aldehyde (0.02 M) in absolute alcohol and was refluxed for 7 h on a water bath. The mixture was cooled, the solid separated was filtered and crystallized from alcohol.

The preparation of hydrazides and their Schiff base, are schematically shown as under:

Fatty acid hydrazides; B- Thiosemicarbazide; C- 2-alkyl-N-benzylidenehydrazinecarbothioamide

Expression, \( \theta = 1 - \left( \frac{W_i}{W_o} \right) \) was used to determine degree of surface coverage (\( \theta \)). Corrosion rate in mg/cm\(^2\)/h was also calculated.

Characterization of of Schiff bases

Infrared (IR) spectra of all Schiff bases were recorded by FTIR- 8201 PC (Shimadzu) infrared spectrophotometer in KBr.

Results and Discussion

Melting points for Schiff bases are observed in the following order: BK\(_1\) > BR\(_1\) > BN\(_1\) (Table 2). Found
nitrogen contents for BN₁, BR₁ and BK₁ are quite close to theoretical values. All these compounds inhibit corrosion of MS in 1 N HCl solution (Table 3) at all concentrations (100-500 ppm). Inhibition efficiency for all these compounds increased with increase in concentration (Fig. 1). Increased inhibitive action with increase in concentration of inhibitor can be ascribed to blocking of active sites of metal surface

All compounds (BN₁, BR₁ and BK₁) show increase in IE (Fig. 2) with increase of immersion time (3-24 h). This shows persistency of adsorbed schiff bases over a longer test period. For (6 – 24 h) immersion time period BN₁ exhibited substantial rise in IE up to 9 h after which marginal increase in IE was observed. BK₁ recorded appreciable rise in IE up to 12 h immersion time after which the rise in IE with time almost became flat.

IE increases with increase in acid concentration up to 3 N HCl for all Schiff bases tested (Fig. 3). Further, increase in acid concentration up to 5 N HCl causes decrease in IE for all schiff bases, may be due to increased aggressiveness of the acid

With increase in temperature (30-40°C) a significant increase in IE has been observed for BN₁, BR₁ and up to 50°C for BK₁ whereas BR₁ shows minimum increase in IE. Beyond 50-60°C, decrease in IE for all schiff bases, may be due to increased aggressiveness of the acid

Spectral analysis of Schiff bases
IR spectra of Schiff bases of all three oils (Figs 5-7) showed the characteristic band at 3674 cm⁻¹ for OH group and at 3459, 3374 and 3237 cm⁻¹ for primary and secondary NH₂ group. A stretching at 2955, 2918 and 2849 cm⁻¹ was observed for CH₃, CH₂ and CH stretching vibration. A band at 1738 cm⁻¹ for C=O was observed for Ketone stretching vibration. 720-690 cm⁻¹ frequency was observed for Ar-C-H-S bending vibration.

<table>
<thead>
<tr>
<th>Sample</th>
<th>M.W</th>
<th>Melting point°C</th>
<th>% Yield</th>
<th>Nitrogen content, %</th>
<th>Calculated</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>BN₁</td>
<td>443.69</td>
<td>111</td>
<td>52.3</td>
<td>9.47</td>
<td>8.43</td>
<td></td>
</tr>
<tr>
<td>BR₁</td>
<td>443.69</td>
<td>104</td>
<td>48.4</td>
<td>9.47</td>
<td>7.88</td>
<td></td>
</tr>
<tr>
<td>BK₁</td>
<td>443.69</td>
<td>113</td>
<td>57.8</td>
<td>9.47</td>
<td>10.23</td>
<td></td>
</tr>
</tbody>
</table>

BN₁ = 2-alkyl-N-benzylidenehydrazinecarbothioamide of neem oil; BR₁ = 2-alkyl-N-benzylidenehydrazinecarbothioamide of rice bran oil; BK₁ = 2-alkyl-N-benzylidenehydrazinecarbothioamide of karanja oil;

<table>
<thead>
<tr>
<th>Inhibitor conc.</th>
<th>Weight loss for BN₁, BR₁ &amp; BK₁ of (mg)</th>
<th>Inhibition efficiency (IE) for BN₁, BR₁ &amp; BK₁ of %</th>
<th>Corrosion rate (CR) for BN₁, BR₁ &amp; BK₁ of mg/cm²/h</th>
<th>Surface coverage (θ) for BN₁, BR₁ &amp; BK₁ of</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCL</td>
<td>49.1 49.1 49.1</td>
<td>1.2786 1.2786 1.2786</td>
<td>--- --- ---</td>
<td>--- --- ---</td>
</tr>
<tr>
<td>100</td>
<td>20.8 35.7 38.5</td>
<td>0.5417 0.9297 1.0026</td>
<td>0.5764 0.2729 0.2159</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>20.6 32.8 28.3</td>
<td>0.5365 0.8542 0.7370</td>
<td>0.5804 0.3320 0.4236</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>8.5 8.4 23.0</td>
<td>0.2214 0.2187 0.5990</td>
<td>0.8269 0.8289 0.5316</td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>7.0 5.2 15.1</td>
<td>0.1823 0.1354 0.3932</td>
<td>0.8574 0.8941 0.6925</td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>6.8 0.9 9.2</td>
<td>0.1771 0.0234 0.2396</td>
<td>0.8615 0.9817 0.8126</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1—Variation of inhibition efficiency with inhibitor concentration for 100-500 ppm concentration of inhibitors

Fig. 2—Variation of inhibition efficiency with immersion time in 1 N HCl for 500 ppm concentration of inhibitors
Application of adsorption isotherm

In order to understand the mechanism of corrosion inhibition the adsorption behaviour of the organic adsorbate on the metal surface must be known. At any instant a fraction \( \theta \) of the metal surface is covered by the inhibitor molecules and the uncovered fraction \( (1 - \theta) \) reacts with acid as it does in the absence of inhibitor. The surface coverage \( \theta \) values are very useful in explaining the adsorption characteristics. The surface coverage increases thereby increasing the percentage inhibition. To examine the adsorption behaviour of the inhibitor, the data were fitted to the various isotherms. A plot of \( \theta \) versus Log \( C \) was a straight line supporting the monolayer adsorption of the inhibitor (BN\(_1\), BR\(_1\), BK\(_1\)) on the metal surface (Fig. 8). The applicability of Temkin’s adsorption isotherm verifies the assumption of monolayer adsorption on a uniform, homogeneous metal surface with an interaction in the adsorption layer\(^{31}\).
Fig. 6—IR spectrum of BR$_1$ of rice bran oil

Fig. 7—Shows the IR spectrum of BK$_1$ of karanja oil
Kinetic treatment of weight loss results with inhibitor

Activation energy, $E_a$ (kJ/mol) at 303 and 313 K for 500 ppm concentration of inhibitor was calculated using Arrhenius equation

$$k = A e^{-Ea/RT} \quad \ldots (2)$$

where $k$ is specific first order rate constant (h$^{-1}$), $A$ is Arrhenius frequency factor, $R$ is universal gas constant (8.314 J/mol/K) and $T$ is temperature in K. Taking natural logarithm of Eq. (2) and after rearrangement gives

$$E_a = [19.14 T_1 T_2 (\log k_{313} – \log k_{303})] /1000 (T_2 – T_1) \quad \ldots (3)$$

$T_2$ represents 313 K while $T_1$ represents 303 K with the corresponding rate constants $k_{313}$ and $k_{303}$.

$E_a$ value obtained for MS-HCl systems without inhibitors was 15.66 kJ/mol. BR$_1$ exhibited average $E_a$ value of 25.84 kJ/mol, while BN$_1$ and BK$_1$ displayed only 13.54 kJ/mol, -36.69 kJ/mol respectively indicating BR$_1$ as a better inhibitor than BN$_1$ and BK$_1$ (Table 4). MS is, therefore, expected to be more protected in BR$_1$-HCl system and for longer period than in BN$_1$-HCl and BK$_1$-HCl system.

A low activation energy means a fast reaction and a high activation energy means a slow reaction$^{33}$. A high activation energy corresponds to a reaction rate that is very sensitive to temperature. Conversely a small activation energy indicates a reaction rate that varies only slightly with temperature$^{33}$. If a reaction has zero activation energy its rate is independent of temperature. In some cases activation energy ($E_a$) is found negative which indicates that the rate decreases when temperature is raised and such a behaviour is a signal that the reaction has a complex mechanism.

From the value of $Q_A$ given in Table 5, it is assumed the inhibitor is adsorbed on the metal surface in the form of monolayer film, covering at any instant fraction $\theta$, of the metal surface in a uniform random manner, then the heat of adsorption $Q_A$ of the inhibitor can be calculated with the help of the equation$^{35}$:

$$Q_A = 2.303 \times (T_1 T_2 / T_2 – T_1) \left[ \log \left( \left(W_o^* – W_i^*/W_i^* \right) / \left(W_o – W_i / W_i \right) \right) \right] \quad \ldots (4)$$

where, $W_o^*$ is weight loss in uninhibited acid and $W_i^*$ is weight loss in inhibited acid solutions and $W_o$ is weight loss in uninhibited acid and $W_i$ is weight loss in inhibited acid solutions by the inhibitor at Kelvin temperatures $T_2$ and $T_1$, respectively.

The values of the free energy $\Delta G^0$ less than -40 kJ/mol (-9.56 kcal/mol) indicated that the tested Schiff bases are physically adsorbed on the metal surface$^{36}$. The low and negative value of $\Delta G^0$ indicates the spontaneous adsorption of inhibitor on the surface of mild steel$^{37}$. It was also found that
values of activation energy of the inhibited systems were lower than that of uninhibited system. Putilova\textsuperscript{6} indicated that this type of inhibitor is effective at higher temperatures. The values of adsorption $\Delta G^o$ were calculated from the equation\textsuperscript{34}:

$$\Delta G^o = 2.303 \times R \times T \log \frac{C_{\text{inh}} - \log (W_o - W_i/W_i)}{1 - \log (W_o - W_i/W_i) - 1.75}$$

(5)

where, $R$ is a constant (1.987), $T$ is temperature (K), $C$ is concentration of inhibitor in mol/L.

The values of the entropy of activation $\Delta S^o$ indicates the system is entropic controlled. $\Delta S^o$ were calculated from the equation\textsuperscript{35}:

$$\Delta S^o = \frac{Q_A - \Delta G}{T}$$

(6)

where, $Q_A$ is heat of adsorption, $T$ is temperature (K) and $\Delta G^o$ is free energy.

Comparison of corrosion inhibition behaviour of BN$_1$, BR$_1$ and BK$_1$

Using Temkin’s adsorption isotherm\textsuperscript{38}, chemical adsorption is followed by inhibitors (Fig. 8). However, average $E_a$ values for BN$_1$ (13.54 kJ/mol), BR$_1$ (25.84 kJ/mol) and BK$_1$ (-36.69 kJ/mol) are within the range for physical adsorption, and less than 80 kJ/mol expected for chemisorption\textsuperscript{39}. This observation suggests that initial adsorption exhibited by all inhibitors was probably physical where multi layer formation was obtained but as adsorption bonds became stronger with increase in temperature, inhibitors then exhibited chemical adsorption resulting in mono molecular layer formation and better protection for MS. BR$_1$ is more soluble in 1 N HCl than BN$_1$ and BK$_1$, therefore is expected to be present at higher concentrations than BN$_1$ and BK$_1$ in the solution. Difference\textsuperscript{40} in inhibitory properties of inhibitor is closely related to the difference in molecular structures and solubility.

**Conclusions**

Schiff bases of neem, rice bran, and karanja showed good performance as corrosion inhibitors in hydrochloric acid media. All the Schiff bases inhibit corrosion by adsorption mechanism and the adsorption of the compounds from acid solution follow Temkin’s adsorption isotherm. IE increases with increasing inhibitor concentration.

Activation energy calculated in the absence and presence of inhibitor reveal the efficiency of the inhibitor. Higher values of thermodynamic activation function ($E_a$) for inhibited system than those in free acid solution indicate that all inhibitors are more effective at room temperature.

The lower value of heat of adsorption ($Q_A$) for these inhibitors shows physical nature of adsorption and lower value of $\Delta G^o$ indicates that the inhibitor are physically adsorbed on the metal surface and negative value of $\Delta G^o$ indicates the spontaneous adsorption of inhibitor on the surface of mild steel. The entropy of activation $\Delta S^o$ in the absence and presence of the inhibitors are large and negative. This indicates that the activated complex in the rate determining step represents an association rather than dissociation. All the compounds examined acted as mixed inhibitors in HCl.
References