

## Inhibition of corrosion of mild steel by Phenyl thiosemicarbazides of nontraditional oils

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*Received 06 June 2008; revised 18 December 2008; accepted 26 December 2008*

Thiosemicarbazide of phenyl hydrazides of fatty acids 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 phenyl hydrazides derivatives on MS surface in acid solution obeyed Langmuir'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. Activation energies ( $E_a$ ) have been calculated to investigate mechanism of corrosion inhibition.

**Keywords:** Corrosion inhibition, Mild steel, Nontraditional oils, Phenyl thiosemicarbazides

### Introduction

Hydrazides are important starting materials for a wide range of derivatives used as pharmaceutical products, corrosion inhibitors (CIs) and surfactants. Several triazole derivatives obtainable from hydrazides exhibit corrosion inhibition<sup>1</sup> and antibacterial<sup>2</sup> and insecticidal activities<sup>3,4</sup>. Organic compounds containing nitrogen (N), sulphur (S) and/or oxygen (O) atoms are used as inhibitors of acid corrosion<sup>5-10</sup>. Corrosion inhibition in acid medium of mild steel (MS), which is extensively used as fabrication material in sugar, petrochemical, food, paper and textile industries, has been studied<sup>11-13</sup>. Organic compounds are widely used in various industries as CIs in acidic environments<sup>14-15</sup>. CIs derived from fatty acids constitute an important and potential class of inhibitors<sup>16-18</sup>. Up gradation and utilization of non-traditional oils has been subject of various investigative studies<sup>19-23</sup>. Also, studies<sup>24-25</sup> have been carried out on development of oleo chemicals as acid CIs.

This study presents CI behaviour of phenyl thiosemicarbazides of neem oil (PN<sub>3</sub>), rice bran oil (PR<sub>3</sub>)

and karanja oil (PK<sub>3</sub>), on corrosion of MS in HCl solutions.

### Materials and Methods

#### Materials

Oils were procured from Mahavir oil industries Ltd, Mahemdavad, Gujarat, India. Physico-chemical analysis of neem, rice bran and karanja by standard BIS methods<sup>26</sup> gave, respectively: sp gr<sup>25°C</sup>, 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<sup>25°C</sup>, 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<sup>27</sup> (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 (wt%: C, 0.084; Mn, 0.34; Si, 0.13; P, 0.037; S, 0.095; and remainder iron) with a hole (diam, 3 mm) near upper edge have been used for corrosion inhibition study.

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Table 1—Fatty acid composition of oils

Fatty acid	Oils, %		
	Neem	Rice bran	Karanja
Palmitic	16.96	18.50	10.95
Stearic	16.39	2.50	6.57
Oleic	49.31	43.00	57.30
Linoleic	13.95	32.00	17.74
Linolenic	1.85	2.20	2.85
Arachidic	1.54	1.80	4.59

### Methods

#### Preparation of Mixed Fatty Acids from Oil

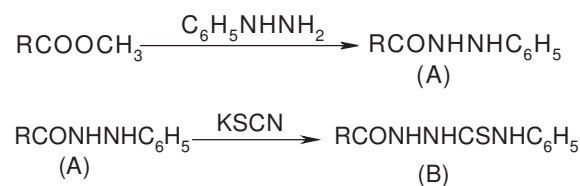
Using saponification method, oil (100 g) was taken in 500 ml round bottom flask and alcoholic NaOH (30%) was added. Contents were refluxed for 3 h on water bath. At the end of reaction, excess alcohol was distilled off and soap was dissolved in hot water. Then, fatty acids were liberated by acidifying soap solution with 1:1 H<sub>2</sub>SO<sub>4</sub> (added till development of red colour in methyl red), washed and dried over anhydrous sodium sulfate.

#### Preparation of Phenyl Hydrazides<sup>28</sup>

Fatty acids (1 g) were dissolved in phenyl hydrazine (2 ml) and solution was boiled gently for 20 min. Upon cooling, solid product precipitated out in good yield by addition of petroleum ether (40-60°C). Precipitate was filtered off with suction and washed with small quantity of petroleum ether until crystals were completely white. These crystals were recrystallised from alcohol or alcohol-water mixture.

#### Preparation of Phenyl Thiosemicarbazide<sup>29</sup>

To a solution of a 0.02 M phenyl hydrazide in methanol (50 ml), a solution of 0.03 M potassium thiocyanate and HCl (3 ml) was added with constant stirring. Mixture was immediately evaporated to dryness on a steam bath and heated for 1 h with another 50 ml ethanol. The resulting solid was treated with water, and with little ethanol and recrystallised from ethanol.



A- Phenyl hydrazides; B- Phenyl thiosemicarbazide

### Weight Loss Studies

MS coupons (3 cm x 1 cm x 0.05 cm) were polished with different grade of emery papers, degreased with

acetone, washed thoroughly with conductivity water and finally dried in air. Coupons were weighed and suspended vertically in aerated unstirred 1 N HCl (150 ml) with and without inhibitor for 6 h. Coupons were removed from solution and cleaned by brushing under running tap water to remove corrosion products, dried and reweighed to determine weight loss<sup>30</sup>. In each case, triplicate experiments were performed. Inhibition efficiency IE (%) was calculated as

$$\text{IE} = 100 \times (\text{W}_o - \text{W}_i) / \text{W}_o \quad \dots(1)$$

where W<sub>o</sub> and W<sub>i</sub> are weight losses in uninhibited and inhibited corroding solutions respectively. Expression,  $\theta = 1 - (\text{W}_i / \text{W}_o)$  was used to determine degree of surface coverage ( $\theta$ ). Corrosion rate in mg/cm<sup>2</sup>/h was also calculated.

### Characterization of Phenyl Thiosemicarbazides

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

### Results and Discussion

Melting points for PTs are observed in the following order: PN<sub>3</sub> > PR<sub>3</sub> & PK<sub>3</sub> (Table 2). Nitrogen contents for PN<sub>3</sub>, PR<sub>3</sub> and PK<sub>3</sub> are quite close. All these compounds inhibit MS corrosion in 1 N HCl (Table 3) at all concentrations (100-500 ppm). IE 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<sup>31</sup>.

With increase in temperature (30-50°C), a significant increase in IE was observed of PN<sub>3</sub> and PR<sub>3</sub>, whereas minimum increase was recorded of PK<sub>3</sub>. Beyond 50-60°C, decrease in IE was observed for all

Table 2—Analysis of phenyl thiosemicarbazides derivatives

Sample	Melting point, °C	Yield %	Nitrogen content %	
			Calculated	Found
PN <sub>3</sub>	86	80.8	9.73	10.84
PR <sub>3</sub>	82	82.3	9.73	11.80
PK <sub>3</sub>	82	81.3	9.73	9.98

PN<sub>3</sub> = Phenyl thiosemicarbazide of neem oil; PR<sub>3</sub> = Phenyl thiosemicarbazide of rice bran oil; PK<sub>3</sub> = Phenyl thiosemicarbazide of karanja oil

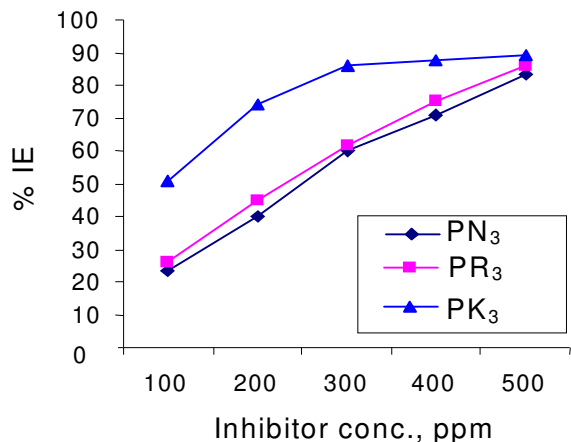


Fig. 1—Variation of inhibition efficiency with inhibitor concentration (100-500ppm) of inhibitors

compounds, may be due to decomposition of hydrophobic long chain (Fig. 2a). All compounds (PN<sub>3</sub>, PR<sub>3</sub> and PK<sub>3</sub>) show increase in IE (Fig. 2b) with increase of immersion time (3-24 h). This shows persistency of adsorbed PTs over a longer test period. IE increases with increase in acid concentration up to 3 N HCl for all PTs tested (Fig. 2c). Further, increase in acid concentration up to 5 N HCL causes decrease in IE for all PTs, may be due to increased acid aggressiveness<sup>32</sup>.

#### Spectral Analysis of Phenyl Hydrazides and Phenyl Thiosemicarbazides

IR spectra of phenyl hydrazides of all three oils showed characteristic band at 2920 cm<sup>-1</sup> for NH group and at 2850 cm<sup>-1</sup> for CH<sub>2</sub> stretching vibration. A stretching at 3293 cm<sup>-1</sup> was observed for CH=CH stretching vibration. IR spectra of PTs of all three oils (Fig. 3) showed characteristic band at 2920 cm<sup>-1</sup> for NH group and at 2850 cm<sup>-1</sup> for CH<sub>2</sub> stretching vibration. A stretching at 3293 cm<sup>-1</sup> was observed for CH=CH stretching vibration. A strong band at 1240-1242 cm<sup>-1</sup> for C=S was observed and absence of any band around 1800-2700 cm<sup>-1</sup>. Aromatic ring had 3290-3294 cm<sup>-1</sup> frequency. Also a strong band for C=N was observed around 1600 cm<sup>-1</sup>.

#### Application of Adsorption Isotherm

At any instant, a fraction  $\theta$  of metal surface is covered by inhibitor molecules and uncovered fraction (1- $\theta$ ) reacts with acid as it does in absence of inhibitor. Surface coverage ( $\theta$  values) increases by increasing percentage inhibition. To examine adsorption behaviour of inhibitor, using Langmuir's adsorption isotherm, a plot of

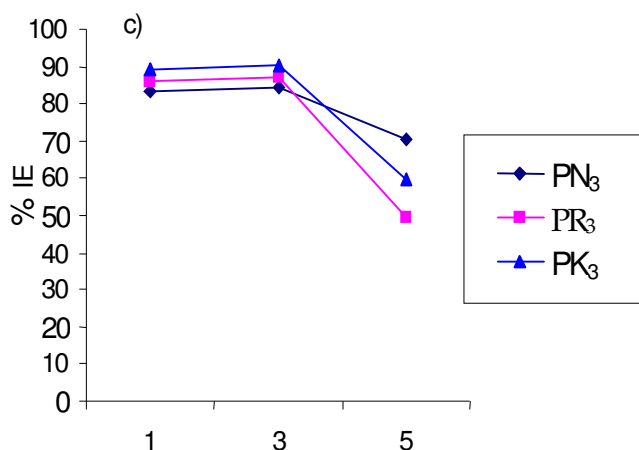
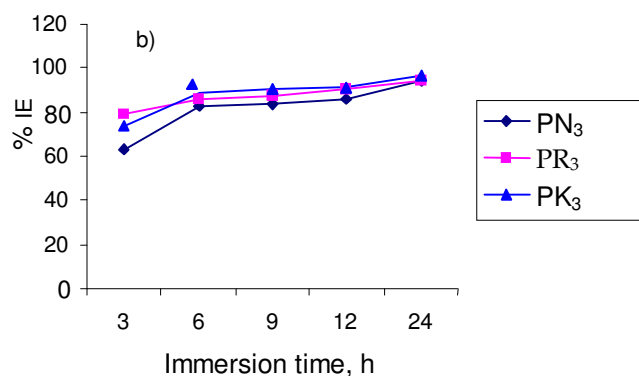
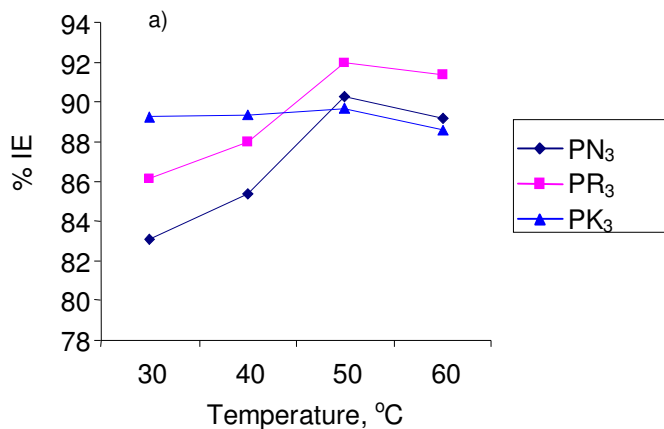


Fig. 2—Variation of inhibition efficiency (inhibitors concentration, 500 ppm) with: a) solution temperature in 1 N HCl; b) immersion time in 1N HCl; and c) acid concentration

Table 3—Effect of phenyl thiosemicarbazide on rate of corrosion of mild steel at 30± 1°C for 6 h

Inhibitor (HCl) conc. ppm	Weight loss for phenyl thiosemicarbazides mg			Inhibition efficiency (IE) for phenyl thiosemicarbazides %			Corrosion rate (CR) for phenyl thiosemicarbazides mg/cm <sup>2</sup> /h			Surface coverage (θ) for phenyl thiosemicarbazides		
	PN <sub>3</sub>	PR <sub>3</sub>	PK <sub>3</sub>	PN <sub>3</sub>	PR <sub>3</sub>	PK <sub>3</sub>	PN <sub>3</sub>	PR <sub>3</sub>	PK <sub>3</sub>	PN <sub>3</sub>	PR <sub>3</sub>	PK <sub>3</sub>
0	65	65	65	—	—	—	1.6927	1.6927	1.6927	—	—	—
100	50	48	32	23.08	26.15	50.77	1.3021	1.2500	0.8333	0.2308	0.2615	0.5077
200	39	36	17	40.00	44.62	73.85	1.0156	0.9375	0.4427	0.4000	0.4462	0.7385
300	26	25	09	60.00	61.54	86.15	1.6771	0.6510	0.2344	0.6000	0.6154	0.8615
400	19	16	08	70.77	75.38	87.69	0.4948	0.4167	0.2083	0.7077	0.7538	0.8769
500	11	09	07	83.08	86.15	89.23	0.2865	0.2344	0.1823	0.8308	0.8615	0.8923

Table 4—Activation energy (E<sub>a</sub>) for mild steel in absence and presence of maximal concentration of the inhibitor

Inhibitor conc. (ppm)	Time h	k <sub>303</sub> h <sup>-1</sup>				k <sub>313</sub> h <sup>-1</sup>				With inhibitor E <sub>a</sub> , KJ/mol		Without inhibitor E <sub>a</sub> , KJ/mol	
		PN <sub>3</sub>	PR <sub>3</sub>	PK <sub>3</sub>	HCL	PN <sub>3</sub>	PR <sub>3</sub>	PK <sub>3</sub>	HCL	PN <sub>3</sub>	PR <sub>3</sub>	PK <sub>3</sub>	HCL
500	3	0.00160	0.00092	0.00068	0.00444	0.00209	0.00154	0.00129	0.00585	21.06	40.61	50.48	21.74
500	6	0.00131	0.00108	0.00077	0.00778	0.00130	0.00106	0.00093	0.00585	0.60	41.74	14.83	10.60
500	9	0.00105	0.00083	0.00061	0.00664	0.00101	0.00076	0.00045	0.00890	3.06	6.95	23.98	4.61
500	12	0.00085	0.00057	0.00051	0.00627	0.00080	0.00040	0.00034	0.00704	4.78	27.92	31.96	4.99
500	24	0.00056	0.00054	0.00034	0.01048	0.00057	0.00052	0.00031	0.00668	1.39	2.98	7.28	3.53
Av E <sub>a</sub> value										6.18	24.04	25.71	9.09

k<sub>303</sub> = Rate constant at 303K; k<sub>313</sub> = Rate constant at 313K; E<sub>a</sub> = Activation energy

log (θ/1-θ) versus log C was a straight line supporting monolayer adsorption of inhibitor on the metal surface (Fig. 4).

#### Kinetic Treatment of Weight Loss Results with Inhibitor

Activation energy, E<sub>a</sub> (KJ/mol) at 303 and 313 K for 500 ppm concentration of inhibitor was calculated using Arrhenius equation

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

where k is specific first order rate constant (h<sup>-1</sup>), A is Arrhenius frequency factor, R is universal gas constant (8.314 J/mol/K) and T is temperature in K. Natural logarithm of Eq. (2) gives

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

T<sub>2</sub> represents 313 K while T<sub>1</sub> represents 303 K with corresponding rate constants k<sub>313</sub> and k<sub>303</sub>. E<sub>a</sub> value obtained for MS-HCl systems without inhibitors was 9.09 KJ/mol. Average E<sub>a</sub> value of PK<sub>3</sub> (25.71 KJ/mol) was higher than that of PR<sub>3</sub> (24.04 KJ/mol) and PN<sub>3</sub> (6.18 KJ/mol), indicating PK<sub>3</sub> as a better inhibitor than PN<sub>3</sub> and PR<sub>3</sub><sup>33</sup> (Table 4). MS is, therefore, expected to be more protected in PK<sub>3</sub>-HCl system and for longer period than in PR<sub>3</sub>-HCl and PN<sub>3</sub>-HCl system.

#### Comparison of Corrosion Inhibition Behaviour of PN<sub>3</sub>, PR<sub>3</sub> and PK<sub>3</sub>

Using Langmuir adsorption isotherm<sup>34</sup>, chemical adsorption is followed by inhibitors (Fig. 4). However, average E<sub>a</sub> values for PN<sub>3</sub>, PR<sub>3</sub> and PK<sub>3</sub> are within the range for physical adsorption, and less than 80 KJ/mol expected for chemisorption<sup>35</sup>. This observation suggests

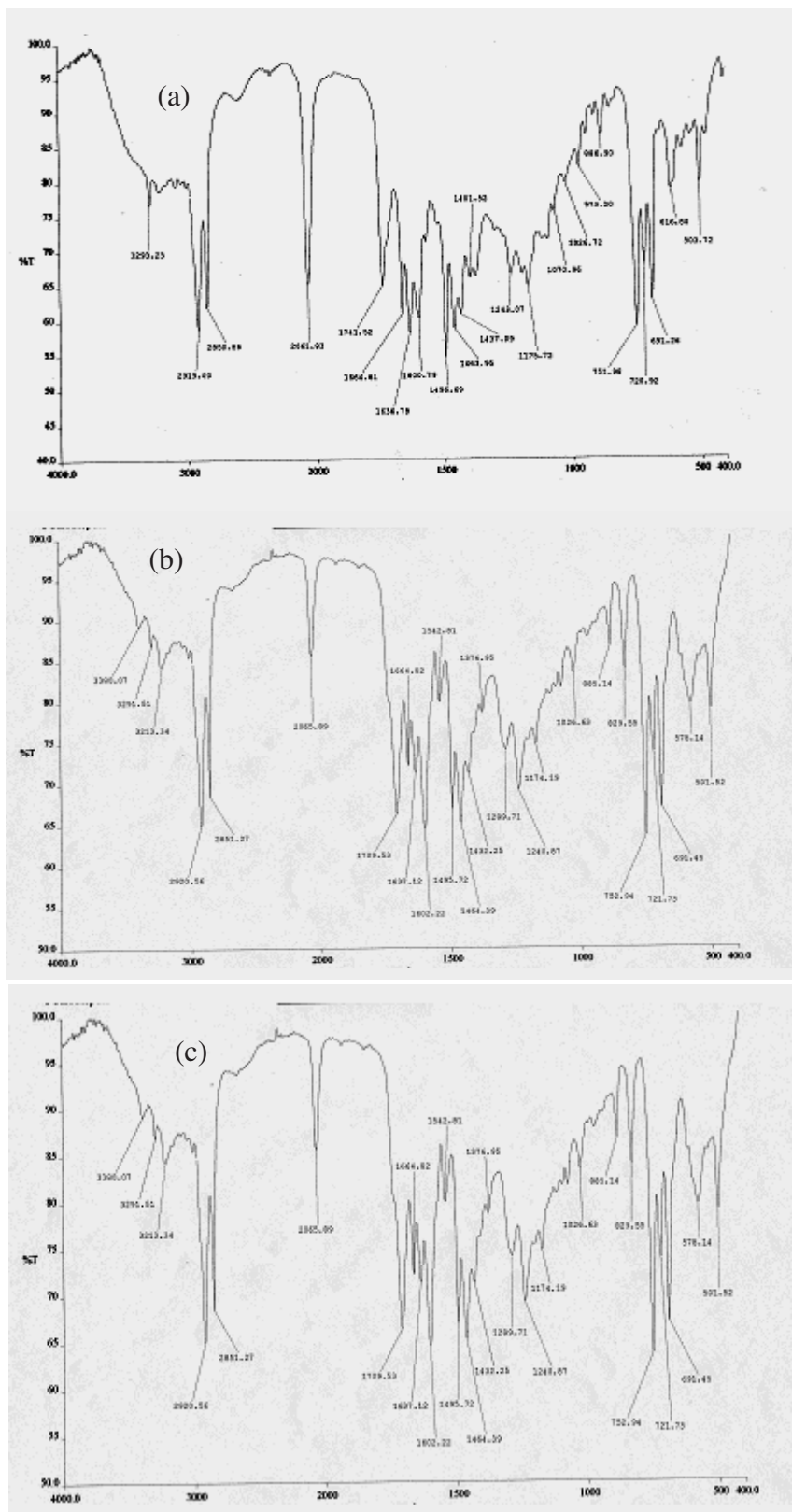


Fig. 3—IR spectrum of: a) PN<sub>3</sub>; b) PR<sub>3</sub>; c) PK<sub>3</sub>

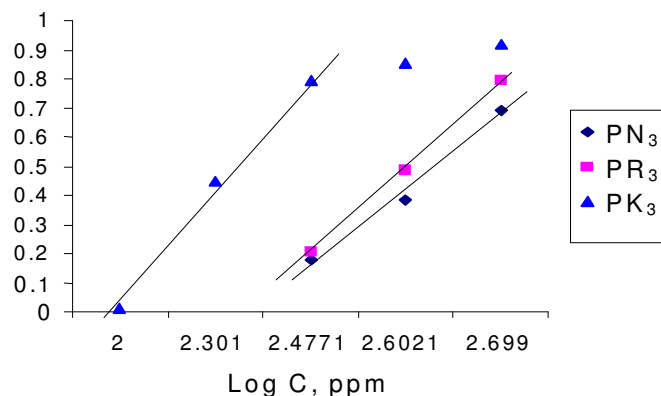


Fig. 4—Langmuir's adsorption isotherm for adsorption of various inhibitors in 1 N HCl on the surface of mild steel

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 exhibited chemical adsorption resulting in mono molecular layer formation and better protection for MS. PK<sub>3</sub>, being more soluble in 1 N HCl than PR<sub>3</sub> and PN<sub>3</sub>, is expected to be present at higher concentrations than PR<sub>3</sub> and PN<sub>3</sub> in the solution. Difference<sup>36</sup> in inhibitory properties of inhibitor is closely related to the difference in molecular structures and solubility.

### Conclusions

PTs of neem, rice bran, and karanja showed good performance as corrosion inhibitors in HCl media. Order of IE (%) of PTs is PK<sub>3</sub> > PR<sub>3</sub> > PN<sub>3</sub>. Adsorption of all PTs from acid solution followed Langmuir's adsorption isotherm. IE increases with increasing inhibitor concentration. Higher values of thermodynamic activation function ( $E_a$ ) for inhibited system than those in free acid solution except PN<sub>3</sub> indicating that all inhibitors except PN<sub>3</sub> are more effective at room temperature.  $E_a$  value for PN<sub>3</sub> is less than those in free acid indicating that inhibitor exhibits high efficiency at elevated temperature. All PTs of oils acted as mixed inhibitors in HCl.

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