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NOVEL GREEN SOYBEAN OIL DERIVATIVES AS CORROSION INHIBITORS FOR MILD STEEL AT 0.5N HCL

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Abstract

Novel four green corrosion inhibitors were prepared via amination of brominated soybean oil using different types of amines (urea, thiourea, p- toluidine, and 3-amino benzoic acid). The prepared compounds were elucidated using FTIR and ^{1}H NMR; they were evaluated as corrosion inhibitors at different temperatures (308, 318, 328 and 338K) using weight loss method and chemical analysis method. The corrosion tests proved that the prepared compounds exhibit excellent corrosion inhibition properties at acidic medium.

Keywords: Soybean oil; Gabriel synthesis; carbon steel; green corrosion inhibitors; weight loss method; chemical analysis method.

1. Introduction

The soybean seeds are composed of 40% protein and 20% oil content, and most importantly soybean oil accounts for approximately 30% of the world's vegetable oil supply [1]. Although soybean oil is primarily used as edible oil, there is a continuing demand for its use in industrial applications. The fatty acid composition of soybean oil "10.6% palmitic acid; 2.4% stearic acid; 23.5% oleic acid; 51.2% linoleic acid; 8.5% linolenic acid; and 3.8% other" by weight [2].

Corrosion is the damage to metal caused by reaction with its environment. "Damage" is specified purposely to exclude processes, such as chemical milling, anodizing of aluminum, and bluing of steel, which modify the metal intentionally. Rusting is a type of corrosion but it is the corrosion of ferrous metals (irons and steels) only, producing that familiar brownish-red corrosion product, rust. The environment that corrodes a metal can be anything; air, water, and soil are common but everything from tomato juice to blood contacts metals, and most environments are corrosive. Corrosion is a natural process for metals that causes them to react with their environment to form more stable compounds [3].

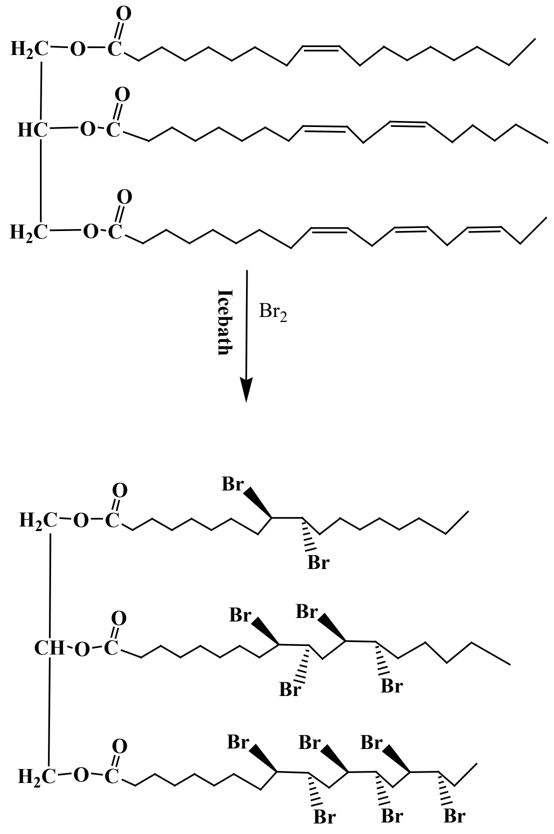
Corrosion inhibitor is a chemical added to the corrosive environment in small amounts to reduce the corrosion rate. Some inhibitors interfere with the anode reaction, some with the cathode reaction, and some with both. They are usually used to prevent general corrosion but most are not effective in preventing localized attack, such as crevice corrosion, pitting, or SCc. Inhibitors generally interact with the metal surface in some way: to form a passive film, to form a barrier film of adsorbed inhibitor that may be only a monolayer or less, or to form a thick barrier layer of reaction products or inhibitor [3-11]. Organic Adsorption Inhibitors that coat metal with an oily surface layer will protect it. The inhibition property of these compounds is attributed to their molecular structure. The planarity and the lone pairs of electrons in the heteroatoms are important features that determine the adsorption of these molecules on the metallic surfaces. They can adsorb on the metal surface, block the active sites on the surface and thereby reduce the corrosion rate. It has been observed that the adsorption of organic inhibitors depends on the electron density of the active part of the molecule such as aromatic rings and heteroatoms [12-15]. These inhibitors are commonly used in acids, although a few function in neutral or alkaline solutions. In adsorbing on the metal, they replace adsorbed water molecules and prevent water from solvating metal ions or prevent H^+ ions from adsorbing at cathode sites where reduction to H_2 (g) could occur [16-17].

In the present work Gabriel method was used for synthesizing of four different types of green aminated soybean derivatives. The prepared compounds were characterized using FTIR, and ^{1}H NMR. The prepared compounds were evaluated as corrosion inhibitors for mild steel at 0.5N HCl by weight loss method and chemical analysis method. The effect of temperature was also studied.

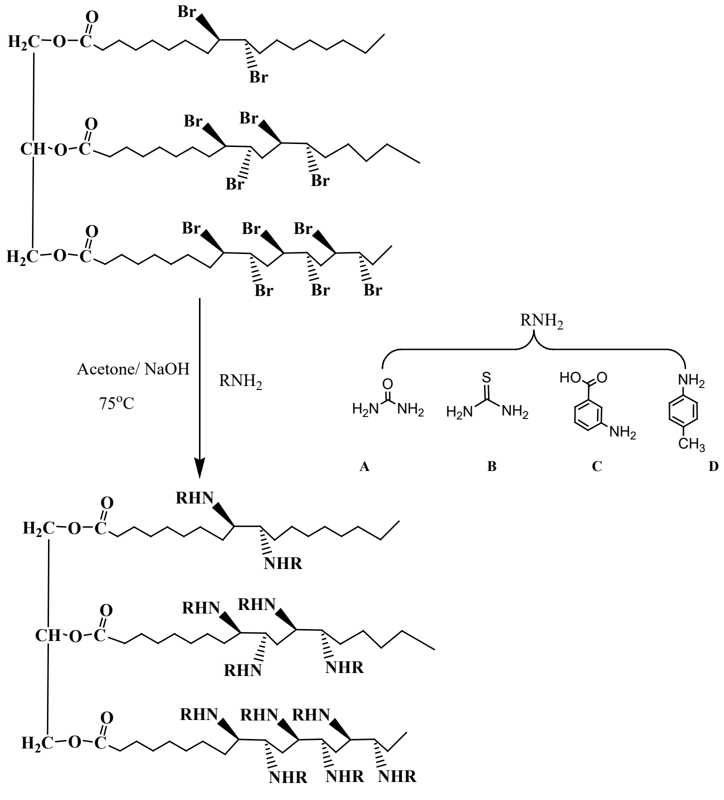
2. Experimental

2.1. Brominating of soybean oil

One mole of soybean oil (878g) was placed in round bottom flask, and six moles of bromine (958.8g) were placed in quick fitted dropping funnel. The bromine solution was allowed to react drop by drop, until the end of bromine addition, with continuous stirring in an ice bath. The obtained product is mentioned at Scheme 1.



Scheme 1. Brominated soybean



Scheme 2. Aminated derivatives of soybean oil.

2.2. Synthesis of novel green corrosion inhibitors based on soybean oil

2.2.1. Synthesis of corrosion inhibitor (S_1)

In 250mL round bottom flask, about (18.368g) of brominated soybean oil, (7.2g) of urea, 10mL of acetone and 3mL of NaOH were placed. The flask was connected with quick fitted condenser and enabled to reflux using heating mantel at 75°C, for 1hr., Scheme 2.

2.2.2. Synthesis of corrosion inhibitor (S_2)

In 250mL round bottom flask, about (18.368g) of brominated soybean oil, (9.13g) of thiourea, 10mL of acetone and 3mL of NaOH were placed. The flask was connected with quick fitted condenser and enabled to reflux using heating mantel at 75°C, for 1hr., Scheme 2.

2.2.3. Synthesis of corrosion inhibitor (S_3)

In 250mL round bottom flask, about (18.368g) of brominated soybean oil, (16.45g) of 3-amino benzoic acid, 10mL of acetone and 3mL of NaOH were placed. The flask was connected with quick fitted condenser and enabled to reflux using heating mantel at 75°C, for 1hr., Scheme 2.

2.2.4. Synthesis of corrosion inhibitor (S_4)

In 250mL round bottom flask, about (18.368g) of brominated soybean oil, (12.85g) of p-toluidine, 10mL of acetone and 3mL of NaOH were placed. The flask was connected with quick fitted condenser and enabled to reflux using heating mantel at 75°C, for 1hr., Scheme 2.

2.3. Elucidation of chemical structure of the prepared compounds

2.3.1. Using FTIR

The prepared compounds were elucidated using Nicolet iS10-FTIR Spectrophotometer, KBr, Jazan University, Saudi Arabia.

2.3.2. Using ^{1}H NMR

The structure of the prepared corrosion inhibitors were elucidated using Proton Nuclear Magnetic Resonance ^{1}H-NMR spectra using a 300 MHz Varian NMR–300 spectrometer using DMSO as a solvent, NCR, Giza, Egypt.

2.4. Corrosion studies

2.4.1. Weight loss measurements

Mild steel coupons having chemical composition mentioned in Table 1, with dimensions 7.0 * 5.0 * 0.3cm were abraded using different grades of emery papers grades (310, 410, and 610), washed with bi-distilled water, degreased with acetone, dried and kept in a desiccator.

Table 1. Constituents of mild steel alloy

Element	C	Mn	P	S	Si	Fe
Ratio (%)	0.11	0.45	0.04	0.05	0.25	99.10

Weigh accurately using a digital balance with high sensitivity. The coupons were immersed in 0.5N HCl solution with and without various concentrations (250, 500, 1000, 2000, and 3000) ppm of the prepared inhibitors, separately for 3 hrs., at different temperatures (308, 318 328 and 338K). Weight loss experiments were carried out according to the ASTM standard procedure described in reference [18]. In brief, mild steel specimens in triplicate were immersed in 100mL 0.5N HCl containing various concentrations of the studied inhibitors. The mass of the specimens before and after immersion was determined using an analytical balance accurate to 0.01mg. Reading were taken after each one hour, the coupons were washed with bi-distilled water, dried and weighed accurately [19-26]. The investigations carried out in the open air. For further data processing, the average of the three replicate values was used. The pre-cleaned and weighed coupons were suspended in beakers containing the test solutions using glass hooks and rods. The weight loss was calculated by the following equation:

$$\Delta W = \mathrm{W1} - \mathrm{W2} \qquad (1)$$

where W_1 and W_2 are the weight of coupons before and after immersion.

The surface coverage area (Θ) for the different concentrations of the prepared corrosion inhibitors in 0.5N HCl was calculated according to the following equation:

$$\theta = 1 - \frac{W1}{W2} \qquad (2)$$

The inhibition efficiency according to weight loss method IE_w (%) was determined by the following equation:

$$IEw\,\% = \frac{(\mathrm{Wcorr})}{\mathrm{W`corr}} * 100 \qquad (3)$$

where W_{corr} and $W`_{corr}$ are the corrosion rate of coupon with and without corrosion inhibitors, respectively.

The corrosion rate (CR) was calculated by the following equation:

$$\mathrm{CR} = \frac{W1-W2}{At} \qquad (4)$$

where W_1 *and* W_2 are the weight of coupons before and after immersion in test solutions; *A* is the total area of the coupon (cm^2); and *t* is the immersion time (h).

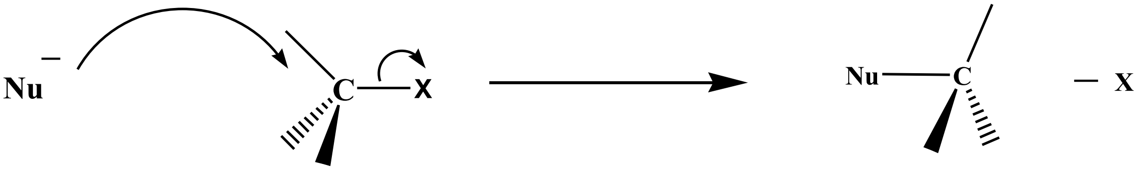
2.4.2. Chemical analysis of solution according to weight loss method

When a metal undergoes corrosion in an electrolyte of a fixed volume, cations of corroding metal will accumulate in solution. Accordingly, the solution becomes more concentrated in the dissolved cation with the progression of time [27]. Thus, chemical analysis of withdrawn aliquots of the solution as a function of time allows determination of the corrosion rate according to equation (5).

$$CR\ Fe\left(\frac{g}{cm2.\ h}\right) = \left(\frac{[Fe+3]mole}{cm2.h}\right)\left(\frac{1\ mole\ Fe}{1mole\ [Fe+3]}\right)\left(\frac{55.85\ g\ Fe}{1\ mole\ Fe}\right) \qquad (5)$$

3. Results and discussion

Electrophiles that have leaving groups (X) attached to C (Sp^3) usually undergo substitution or elimination reactions. In a nucleophilic substitution reaction, a nucleophile – electrophile (σ bond) replaces the electrophile–(X–σ) bond. Substitution reactions at 1° and 2° C (Sp^3) usually proceed by the S_N2 mechanism under basic or neutral conditions. In the S_N2 mechanism, the nucleophile Nu-approaches the electrophilic center opposite X and in line with the C-X bond. The lone pair on–Nu is used to form the–C–Nu bond, and the pair of electrons in the C–bond simultaneously leaves with X as the bond breaks. The other three groups on C move away from Nu and toward X as the reaction proceeds, so that when the reaction is complete, the stereochemistry of C is inverted [28].



3.1. Elucidation of the prepared corrosion inhibitors

The prepared brominated soybean (S) was elucidated using Fourier transform infrared spectroscopy (FTIR), Figure 1. It has two different peaks than soybean oil located at $758cm^{-1}$ corresponding to C – Br, and disappearance of peak at $1638cm^{-1}$ corresponding to C = C bond. FTIR corresponding to the four prepared corrosion inhibitors showed the disappearance of C – Br at $758cm^{-1}$ and appearance of one peak at $3446cm^{-1}$ corresponding to secondary – NH group. The presence of peak at about $1740cm^{-1}$ insures the stability of ester group toward reaction with amines. ^1H NMR analysis of the brominated soybean (S) and the aminated soybean derivatives (S_1-S_4) are mentioned at Table 2.

3.2. Corrosion tests

3.2.1. Weight loss method

The inhibition efficiency of the organic compounds depends on many factors including the number of adsorption sites and their charge density, molecular size, heat of hydrogenation, mode of interaction with the metal surface and formation of metallic complexes [7]. Weight loss parameters were mentioned at Table 3.

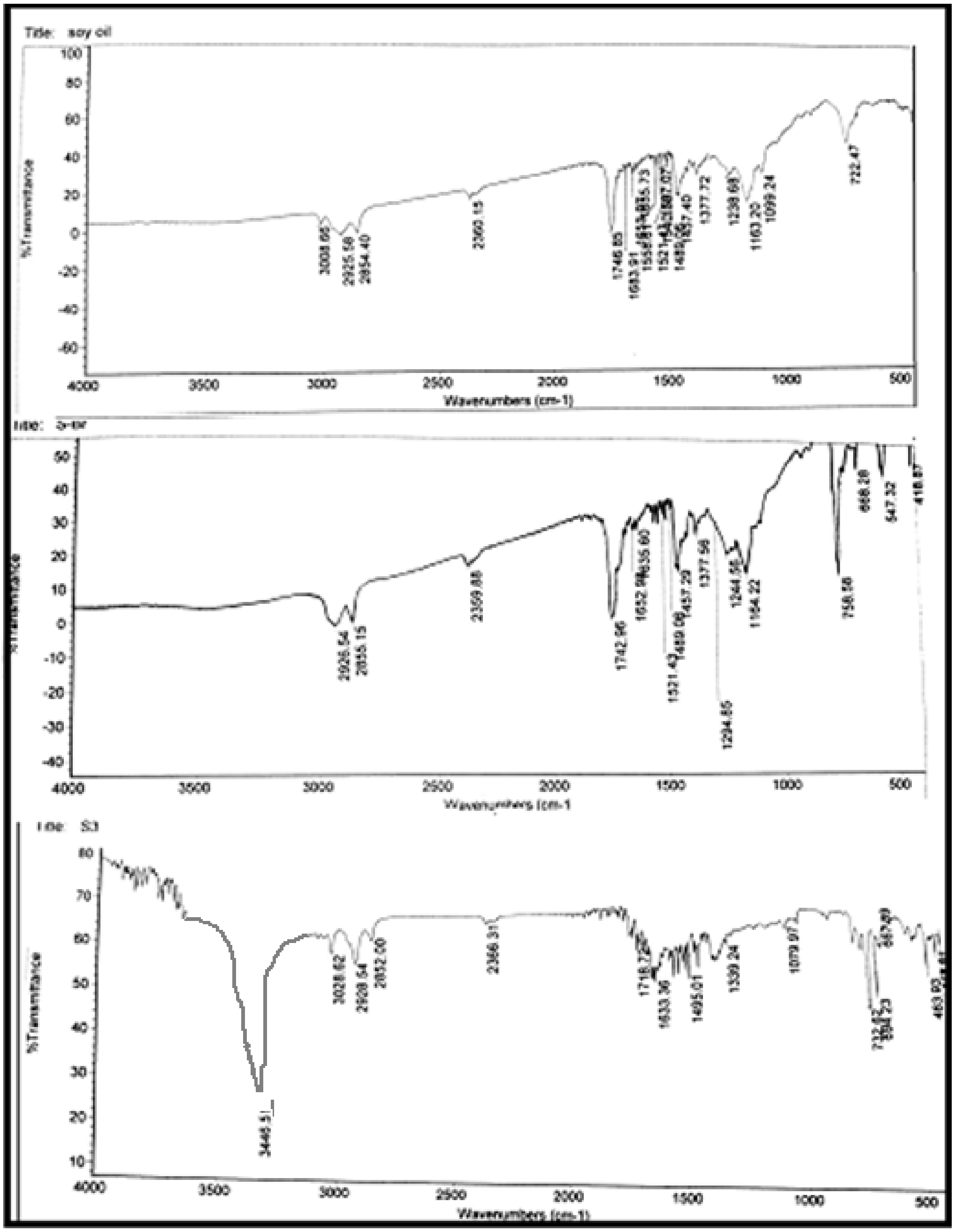


Figure 1. FTIR of soybean oil, brominated soybean, and S_3 aminated derivative of soybean

Table 2. ^1H NMR data of (S) and (S_1-S_4) compounds

Compound digestion	Group	ppm
S	- CH_3 - $(CH_2)n$ - CH_2 - CH - Br - CO- CH_2 - CH- Br - CH_2 –O - CH – O-	0.8 1.29 1.79 2.25 3.38 4.45; 4.20 5.15

Compound digestion	Group	ppm
S_1	- CH_3 - $(CH_2)n$ - CH_2 –O - CH – O- - CH-N- - NH - NH_2	0.96 1.29 4.32 5.15 4.20 6.00 6.00
S_2	- CH_3 - $(CH_2)n$ - CH_2 –O - CH – O- - CH-N- - NH - NH_2 - NC- CH_2 – C-N - CO- CH_2	0.96 1.29 4.32 5.15 2.84 2.00 2.00 1.73 2.25
S_3	- CH_3 - $(CH_2)n$ - CH_2 –O - CH – O- - CO- CH_2 - CH Aromatic - OH	0.96 1.29 4.32 5.15 2.25 6.77 7.25 7.45 11
S_4	- CH_3 - $(CH_2)n$ - CH_2 –O - CH – O- - CO- CH_2 - CH Aromatic - Ph – CH_3 - CH- N	0.96 1.29 4.32 5.15 2.25 6.84; 6.31 2.35 2.84

Table 3. Weight loss parameters

Inhibitor	Concentration "ppm"	Total weight loss (mg)	Corrosion Rate (mg.cm^{-2}.h^{-1})	Surface Coverage (Θ)	IE %
Bank	0	650	6.19	…….	…….
S_1	3000	42.57	0.4054	0.9345	93.45
	2000	54.46	0.5187	0.9162	91.62
	1000	81.24	0.7737	0.875	87.50
	500	95.99	0.9142	0.8523	85.23
	250	100	0.952	0.846	84.62
S_2	3000	33.9274	0.3231	0.9478	94.78
	2000	42.5067	0.4048	0.9346	93.46
	1000	53.56	0.51	0.9176	91.76
	500	63.695	0.6066	0.902	90.20
	250	73.05	0.6957	0.8876	88.76
S_3	3000	29.505	0.281	0.9546	95.46
	2000	32.63	0.3107	0.9498	94.98
	1000	43.87	0.4178	0.9325	93.25
	500	51.996	0.4952	0.92	92%
	250	56.868	0.5416	0.9125	91.25
S_4	3000	21.5783	0.2055	0.9668	96.68
	2000	28.0778	0.2674	0.9568	95.68
	1000	37.827	0.3602	0.9418	94.18
	500	49.00	0.4667	0.9246	92.46
	250	53.68	0.5113	0.9174	91.74

3.2.2. Effect of (S_1-S_4) concentrations

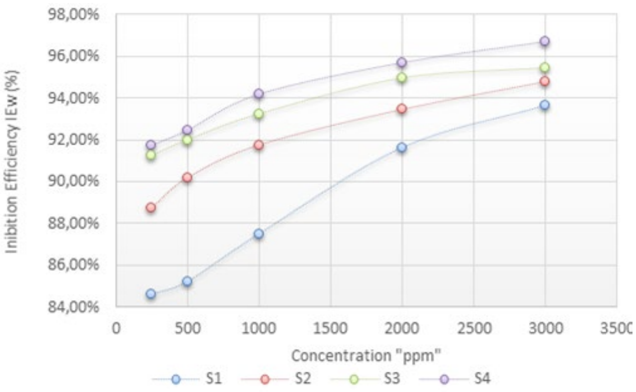


Figure 2. Variation of inhibition efficiency with different concentrations of the prepared inhibitors (S1 – S4) in 0.5N HCl at 308K

The variation of inhibition efficiency (IE_w%) from weight loss measurements with (S_1-S_4) concentrations is shown in Figure 2, while the weight loss parameters; corrosion rate CR, surface coverage Θ, and percentage of inhibition efficiency increases with increasing (S_1-S_4) concentration and record the maximum value (93.63% S_1, 94.78% S_2, 95.46% for S_3 and 96.68% for S_4) of inhibition efficiency at 3000ppm concentration. The inhibition efficiency of the prepared additives increases in the order $S_4 > S_3 > S_2 > S_1$. The highest inhibition efficiency of inhibitor S_4 may be attributed to the presence of (methyl group) electron donating group.

3.2.3. Effect of temperature

In order to calculate the activation energy (Ea) of the corrosion process and investigate the mechanism of inhibition, weight loss measurements were performed in the temperature range of 308-338K in absence and presence of 3000ppm of the prepared inhibitors (S_1-S_4) at 0.5N HCl. It was found that the corrosion rate of mild steel increases with increasing temperature. The results indicates that increasing temperature leads to a decrease of RT, hence increasing the corrosion rate of carbon steel as shown in Figure 3. A plot of ln corrosion rate (ln k) against the reciprocal of absolute temperature (1/T) was drawn graphically to obtain activation energy Ea, according to Arrhenius equation:

$$\ln K = -\frac{Ea}{RT}+constant \qquad (5)$$

where *Ea* equal to slope of this equation.

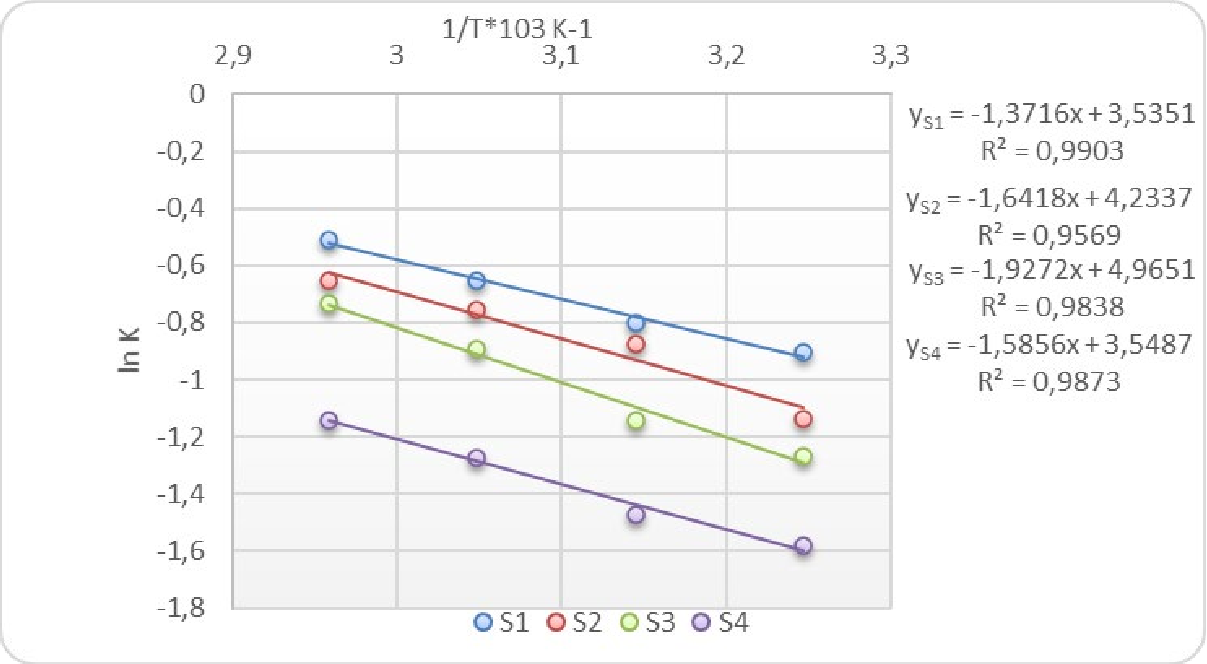


Figure 3. Variation of RT values of carbon steel with 3000ppm of (S1-S4) inhibitors at different tempe-ratures

3.3. Adsorption isotherm

To understand the corrosion inhibition mechanism, the organic compound’s adsorption behavior on the carbon steel surface must be known. The plot of C_{inh}/Θ vs. C_{inh}, Figure 4 yielded a straight line, proved that the adsorption of the prepared corrosion inhibitors from the hydrochloric acid solution obeys Langmuir adsorption isotherm, which is presented by equation (6) [25].

$$\frac{Cinh}{\theta} = \frac{1}{Kads} + Cinh \qquad (6)$$

where C_{inh} is the inhibitor concentration and K_{ads} is the equilibrium constant for the adsorption/desorption process.

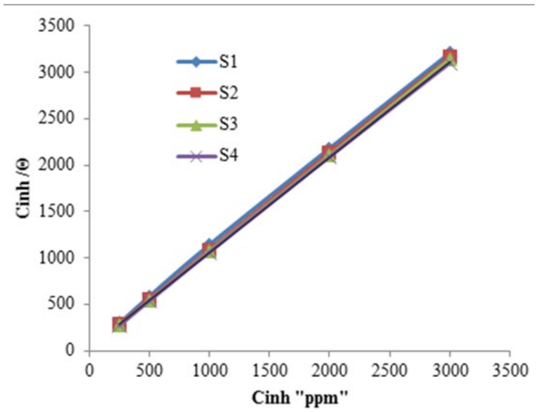


Figure 4. Langmuir isotherms for the adsorption of the prepared corrosion inhibitors on carbon steel surface in 0.5N HCl at 308K

From the intercepts of the straight lines on the C_{inh} / Θ - axis, one can calculate K_{ads}, which is related to the standard free energy of adsorption, ΔG_{ads}, as given by Eq. (7) [26]:

$$\Delta Gads = -RT\,(\ln Kads * 55.5) \qquad (7)$$

The calculated free energy of adsorption (ΔG_{ads}) is given in Table 4. The negative values of ΔG_{ads} indicated that the adsorption of the inhibitors on the metal surface is spontaneous. Generally, values of ΔG_{ads} around 20 kJ mol^{-1} or lower are consistent with the electrostatic interaction between charged molecules and the charged metal surface (physisorption and chemisorption); It can be seen from Table 4 that, calculated *ΔGads* values indicated that the adsorption mechanism of the prepared corrosion inhibitors on carbon steel in 0.5N HCl solution is physical and chemical adsorption. The large values of ΔG_{ads} and its negative sign are usually characteristic of strong interaction and a highly efficient adsorption. The aminated derivatives of soybean oil were generally chemisorbed at the metal surface and displace the adsorbed water and electrolytes from the surface. It is assumed that theseN-containing functional groups act as electron pair donors to the electron depleted dehydrated metal surface. This interaction between the inhibitor and the metal surface is due to the formation of a bond between the N electron pair and the electron cloud at the surface.

Table 4. Adsorption parameters for the prepared corrosion inhibitors (S_1-S_4) on mild steel in 0.5N HCl at 308K.

Inhibitor	K_{ads}	ΔG_{ads} (KJ/mole)
S_1	57.798	-20.34
S_2	30.987	-18.76
S_3	21.706	-17.87
S_4	25.353	-18.261

4. Conclusions

Four green corrosion inhibitors were prepared via reaction of brominated soybean oil with different types of amines "urea, thiourea, 3- amino benzoic acid and p- toluidine". The aminated derivatives were elucidated using FTIR and ^{1}H NMR, and they were evaluated as corrosion inhibitors for mild steel at 0.5N HCl, using weight loss method and chemical analysis method at different temperatures "308-338"K.

It was found that the inhibition efficiency "IE_w%" increases with increasing the inhibitor concentration, while decrease with rising of temperature and the order of increasing the inhibition efficiency "IE_w%" using the prepared corrosion inhibitors was as fellow: $S_1 < S_2 < S_3 < S_4$. The adsorption of the prepared inhibitors on metal surfaces from 0.5N HCl solution obeys

Langmuir adsorption isotherm. The high value of adsorption equilibrium constant suggested that the prepared organic corrosion inhibitors were strongly chemically and physically adsorbed on the mild steel surfaces. Chemical analysis method was used for the determination of weight of the corroded iron according to weight loss calculations and it was found that the amount of the corroded iron decreases with increasing concentration, and the order of increasing the corroded iron was as fellow: $S_1 > S_2 > S_3 > S_4$.

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