JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 16, Preprint 64 submitted 6 November 2013

Carum copticum as an ecofriendly inhibitor for Steel corrosion in 1 M Tartaric acid.

ALKA SINGH* and KALPANA S.
Electrochemistry and Environmental Chemistry Laboratory
Department of Chemistry, Government College,
Kota (Rajasthan) India.
maurya4124@gmail.com
anushrishri@gmail.com

1. Abstract : The influence of a natural aqueous extract of Carum copticum seeds (AECCS) on the corrosion of steel in 1 M Tartaric acid has been studied by weight loss methods. The maximium inhibition efficiency (63.64%) was found at 10% v/v, concentration of inhibitor at 303 K. The effectiveness of the inhibitor increased with the increase in inhibitor concentration. Kinetic and thermodynamic parameters were calculated using Arrhenius equation. Adsorption of the inhibitor on steel surface followed Freundlich adsorption isotherm.

2. Keywords : Corrosion, inhibitors, Steel, Carum copticum, Freundlich adsorption isotherm.

3. Introduction

Steel has been widely used in many industries in handling acidic , alkaline and salt solution. Acids are used especially for cleaning, pickling and descaling [1]. Aqueous solutions of acids are among the most corrosive media. There is a great need to protect steel from dissolution by using corrosion inhibitors. The inhibitive properties of corrosion inhibitors are due to their ability to adsorb on to the electrode surface [2]. Most acid corrosion inhibitors are nitrogen, oxygen and / or sulphur containing organic compounds [3,4]. The main aim of this paper is to study the anticorrosive effect of aqueous extract of Carum copticum seeds (AECCS) on the steel corrosion in 1 M Tartaric acid solutions by using weight loss methods.

Carum copticum seeds contains a volatile oil in which Thymol, γ-Terpinene, p- Cymene, β- Pinene, α – Pinene and Limonene are present [5].

4. Materials & Methodology

Carum copticum seeds were purchased from a local herbal store in Kota. 'R.A. 1-80' variety of *Carum copticum* was taken for experimental purpose.

4.1 Preparation of AECCS

Stock solution of AECCS was prepared by boiling 20 g of dried gounded *Carum copticum* seeds in 250 ml of de-ionized water for 1 hour with an air condenser 1 meter high under low heat. The extract was left over night and then filtered and completed to 250ml by de-ionized water.

4.2 Preparation of aggressive solutions used

The aggressive solutions used were made of AR grade Tartaric acid (E Merck).Standard stock solution of Tartaric acid (1 M) was prepared using de-ionized water.

4.3 Determination of weight loss

A gravimetric technique for weight loss described by Mattsson [6] was adopted to measure the corrosion rates of the specimens. For the weight loss determination, cylindrical steel specimen of 5cm (± 0.02) in length and 1.2 cm in diameter were taken. These specimens were abraded with a series of emery paper then degreased with acetone, washed thoroughly with doubly distilled water and finally dried in hot air for recording their constant weight (m_1) in an electronic balance Citizen model CY 204. Stock solution of aqueous extract of Carum copticum seeds was prepared by boiling 20g of dried grounded Carum copticum seeds in 250ml of de-ionized water for 1 hour with an air condenser 1meter high at low flame. The extract was left over night and then filtered and completed to 1000 ml by de-ionized water. 1M Tartaric acid solutions were used as aggressive solution. The polished specimens were suspended with the help of plastic threads and glass rod in a series of 6 beakers of capacity 200ml each containing 1 M Tartaric acid solution (100ml) in the presence and absence of AECCS. After completion of immersion time, the specimens were taken out, washed, dried, weighed accurately (m_2) and thus subtracting m_2 from m_1 weight loss of steel specimens were determined. The employed concentration range of AECCS was of 0.5 – 10 % (v/v). The immersion time of steel specimen was 1 hour. The experiments were repeated at four different temperatures.

4.4 Determination of corrosion rates & inhibition efficiency

4.4 a.Corrosion rates:

The value of corrosion rate ($\rho_{corr.}$) was calculated from the following equation [7]:

$$\rho_{corr.}\ (\text{g cm}^{-2}\ \text{sec}^{-1}) = \frac{m_1 - m_2}{A \cdot t} \qquad (1)$$

where m_1 and m_2 are the masses of the specimen in aggressive media before corrosion and after corrosion. A is the total area of the specimen and t is the corrosion time.

4.4 b. Inhibition efficiency IE(%):

With the help of calculated corrosion rates, the inhibition efficiency for steel corrosion in Tartaric acid in presence of various concentrations of AECCS and at different temperatures was obtained from the following equation [8] :

$$IE\% = \left(\frac{\rho^{o}_{corr.} - \rho_{corr.}}{\rho^{0}_{corr.}}\right) \times 100 \qquad (2)$$

where $\rho^{0}_{corr.}$ & $\rho_{corr.}$ are the corrosion rates of steel in absence and presence of certain concentration of AECCS respectively.

4.5 Determination of kinetic and thermodynamic parameters

4.5 a. Kinetic parameters:

Kinetic parameters k (rate constant) and B (reaction constant) were calculated with the help of straight lines obtained in graph plotted between log values of inhibitor concentration and log values of corrosion rates at different temperatures.The equation used for determining kinetic parameters is [9,10]:

$$\log \rho_{corr.} = \log k + B \log C_{inh.} \qquad (3)$$

where k is the rate constant and equal to $\rho_{corr.}$ at inhibitor concentration of unity, B is the reaction constant which is a measure for the inhibitor effectiveness and $C_{inh.}$ is the concentration in % (v/v ml/100ml) of the inhibitor.

4.5 b. Thermodynamic parameters:

Energy of activation (E_a)

Energy of activation (E_a) was calculated from the slopes of plots of log ρ versus 1/T and also calculated from following Arrhenius equation [11] :

$$\log \frac{\rho_2}{\rho_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \qquad (4)$$

where ρ_1 and ρ_2 are the corrosion rates at temperatures T_1 and T_2 respectively.

Heat of adsorption ($Q_{ads.}$)

The values of heat of adsorption $Q_{ads.}$ were calculated using the following equation [12] :

$$Q_{ads} = 2.303\ R\ \log \left[\left(\frac{\theta_2}{1-\theta_2} \right) - \left(\frac{\theta_1}{1-\theta_2} \right) \right] \frac{T_1 x T_2}{T_2 - T_1} \qquad (5)$$

where θ_1 & θ_2 are degrees of surface coverage at temperature T_1 & T_2 .

The enthalpy of adsorption ($\Delta H_{ads.}$)

The enthalpy of adsorption ($\Delta H_{ads.}$) was calculated from the following equation [13] :

$$\Delta H_{ads.} = E_a - RT \qquad (6)$$

The positive sign of enthalpies reflect the endothermic nature of the steel dissolution process [5]. The ΔH_{ads} values indicate that the adsorption of inhibitor on metal surface is chemisorption. Physical adsorption occurs in the first stage, then inhibitors are chemisorbed on the metal surface by sharing of an electron pair of heteroatoms present in plant extract with orbital of iron forming covalent bond, leading to the positive value of ΔH_{ads} [14].

5. Results and discussion

5.1 Corrosion rates & inhibition efficiency:

Table.1: Represents the corrosion rates of steel specimen in 1 M Tartaric acid solution in absence and presence of different concentrations of AECCS at different temperatures. A remarkable decrease in steel corrosion rate was observed with the addition of increasing amount of AECCS. It is clear from Table 1. that corrosion rate of steel in 1 M Tartaric acid in absence and presence of AECCS obeys the Arrhenius type reactions as it increases with rising solution temperature.

Fig.1 represents the curves of $\log \rho_{corr.}$ versus $\log C_{inh.}$ at various studied temperature. The straight lines are obtained and the Kinetic parameters (k and B) are calculated by eq. (3) and listed in Table.2.

Table 1. Steel corrosion rates in 1 M Tartaric acid in absence and presence of different concentrations of AECCS at different temperatures

$C_{inh.}$ in % (v/v)	$\rho_{corr.}$ x10^{-8}(g cm^{-2} sec^{-1})			
	30^{0}C	40^{0}C	50^{0}C	60^{0}C
0.0	14.3	24.8	47.5	80.7
0.5	7.2	13.0	21.5	32.5
1.0	6.7	10.5	17.7	28.5
2.0	6.5	9.7	13.8	19.5
5.0	6.0	8.0	10.0	16.2
10.0	5.2	6.5	8.8	13.2

Table 2. Kinetic parameters for the corrosion of steel in 1 M Tartaric acid containing AECCS at different temperatures

Temperature (^{0}C)	Kinetic Parameters	
	B	k x10^{-8} (g cm^{-2} sec^{-1})
30^0	-0.1101	0.6934
40^0	-0.2083	0.4571
50^0	-0.3035	0.3162
60^0	-0.2963	0.3467

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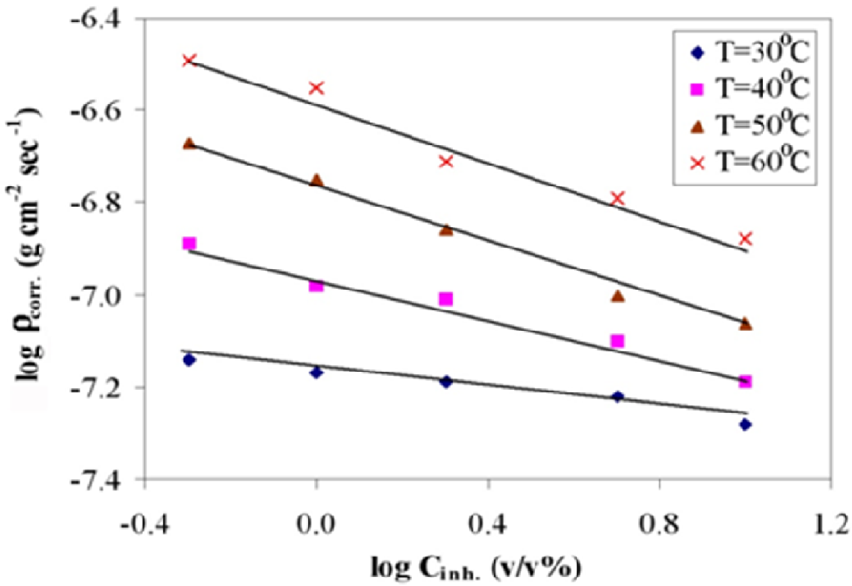

Figure 1. Variation of log $\rho_{corr.}$ with log $C_{inh.}$ for steel in 1 M Tartaric acid in presence of different concentrations of AECCS at different temperatures

5.2 Effect of temperature on inhibition efficiency IE (%)

Table 3. illustrates the variation of IE (%) with AECCS concentration at different temperatures in 1 M Tartaric acid. The obtained data in Table 3. reveal that the inhibition efficiency increases with an increase in the inhibitor concentration. This suggests that the inhibitor species are adsorbed on the steel/ solution interface where the adsorbed species mechanically screen the coated part of the metal surface from the action of the corrosive medium. It can be seen that the IE (%) reaches 63.64% at 303K.

Fig.2. shows the relationship between inhibition efficiency (IE%) and logarithm of concentration (log $C_{inh.}$) of Carum copticum seeds extracts in 1 M Tartaric acid at different temperatures. All plots have the form of S- shaped adsorption isotherm.

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Table 3. Inhibition efficiencies of AECCS at different concentrations & temperatures in 1 M Tartaric acid

$C_{inh.}$ in % (v/v)	IE (%)			
	30^{0}C	40^{0}C	50^{0}C	60^{0}C
0.5	49.65	47.58	54.74	59.72
1.0	53.15	57.66	62.74	64.68
2.0	54.54	60.88	70.94	76.84
5.0	58.04	67.74	78.94	79.92
10.0	63.64	73.79	81.47	83.64

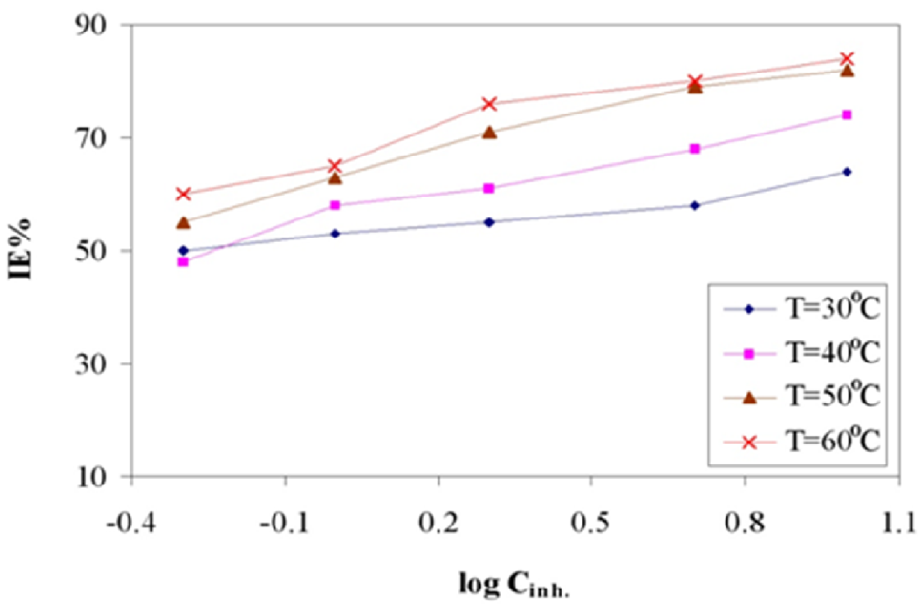

Figure 2. The variation of inhibition efficiency (IE%) of AECCS against log $C_{inh.}$ for steel corrosion in 1 M Tartaric acid at different temperatures

5.3 Adsorption isotherms

Adsorption plays an important role in the inhibition of metallic corrosion by inhibitors. The adsorption of AECCS followed the Freundlich adsorption isotherm using the following equation [15].

$$\Theta = k\,C^{n} \quad (7)$$

$$\log \Theta = \log k + n \log C \quad (8)$$

where $0 < n < 1$, Θ is the degree of surface coverage and is equal to IE%/100, C is the Carum copticum seeds extract concentration and k is the equilibrium constant. The logarithm of degree of surface coverage is plotted against logarithm of inhibitor concentration and straight lines are obtained as a result (Fig.3).

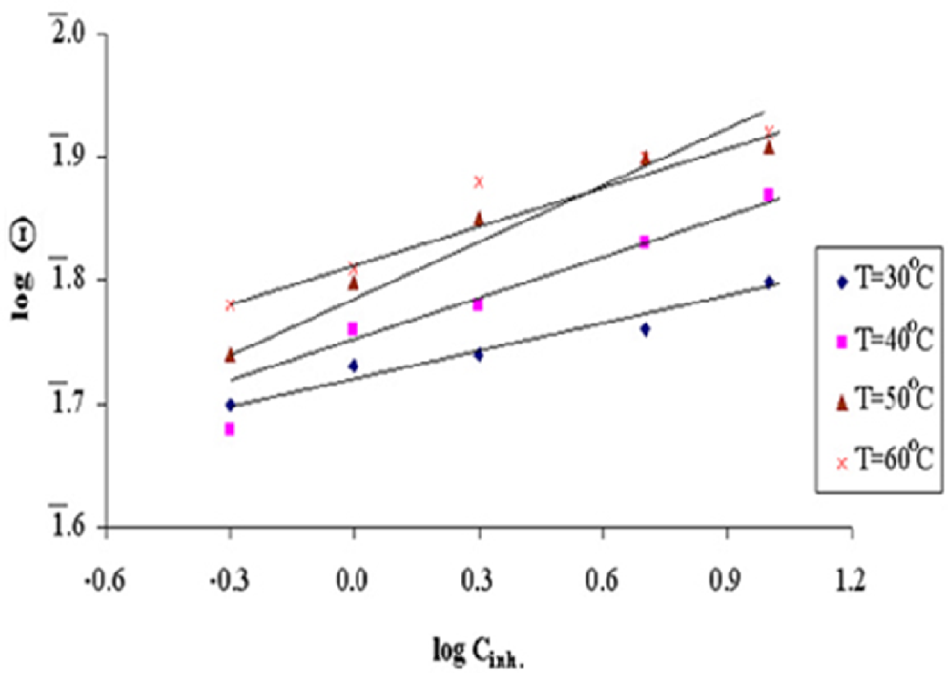

Figure 3. Freundlich adsorption isotherms of AECCS on steel surface in 1 M Tartaric acid at different temperatures

5.4 Thermodynamic consideration

5.4 a. Energy of activation (E_a)

Table 4. shows the calculated values of activation energy (E_a) for steel corrosion in 1 M Tartaric acid with and without inhibitor from 303 K to 333 K. Energy of activation (E_a) was calculated from the slopes of plots of log ρ versus 1/T in Fig

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4. and also calculated from Arrhenius equation (4).The E_a values were found to be 47.94 KJ/mol without AECCS and 25.72 KJ/mol at 10% (v/v) conc. of AECCS. The E_a values calculated from the slopes of Arrhenius plot and by using eq (4) are approximately almost similar.

Table 4. Thermodynamic parameters for steel corrosion in 1 M Tartaric acid with AECCS

Conc. of aqueous extract of Carum copticum seeds (v/v) %	Ea (from Arrhenius eqn.) KJ/mol	Ea (from plot) KJ/mol	$Q_{ads.}$ KJ/mol	$\Delta H_{ads.}$ KJ/mol
0.0	47.94	47.87	-	45.18
0.5	41.75	42.13	-19.57	38.99
1.0	40.10	39.44	-10.09	37.34
2.0	30.44	29.87	18.49	27.68
5.0	27.53	27.38	26.68	24.77
10.0	25.72	25.46	33.91	22.66

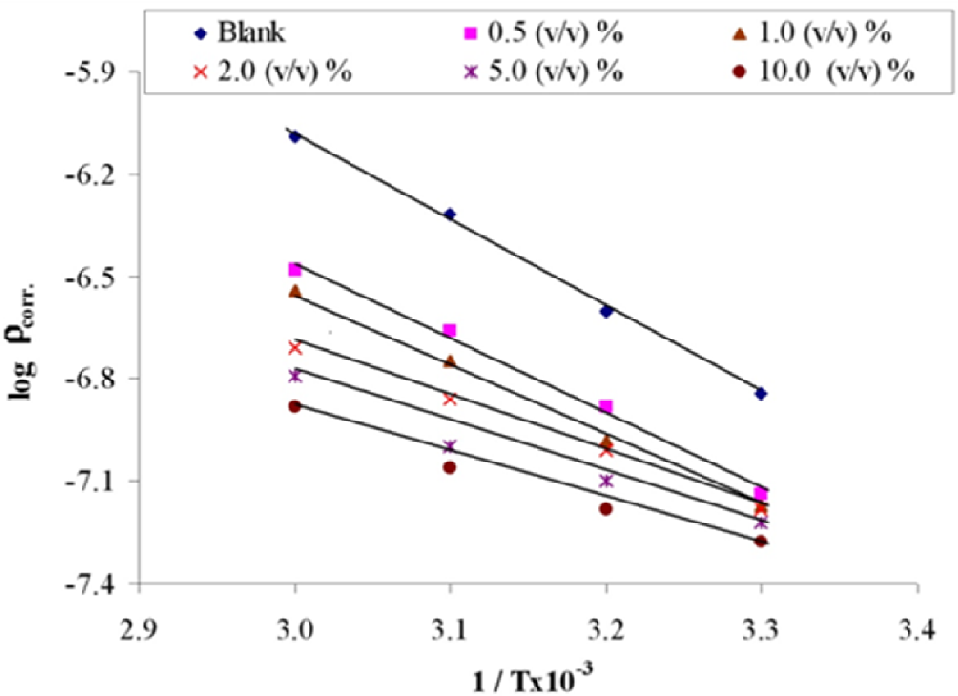

Figure 4. Arrhenius plot for steel corrosion in 1 M Tartaric acid with AECCS

5.4 b. Heat of adsorption (Q_{ads}.)

Table 4. shows the calculated values of heat of adsorption (Q_{ads}.) for steel corrosion in 1 M Tartaric acid at various concentrations of inhibitor. The values of heat of adsorption $Q_{ads.}$ were calculated using equation (5). From Table (4). it is clear that the Q_{ads} values are ranging from -19.57 KJ/mol to 33.91 KJ/mol. The value of $Q_{ads.}$ increases with the increase in concentration of inhibitor.

5.4 c. The enthalpy of adsorption (ΔH_{ads}.)

Table 4. shows the calculated values of enthalpy of adsorption (ΔH_{ads}.) for steel corrosion in 1 M Tartaric acid at various concentrations of inhibitor. The enthalpy of adsorption (ΔH_{ads}.) is calculated using equation (6). From Table (4) it is clear that the ΔH_{ads} is 45.18 KJ/mol in absence of inhibitor and 22.66 KJ/mol at 10% (v/v) concentration of inhibitor at 333 K. The positive sign of enthalpies reflect the endothermic nature of the steel dissolution process [5]. The ΔH_{ads} values indicate that the adsorption of AECCS on steel surface is chemisorption. Physical adsorption occurs in the first stage, then inhibitors are chemisorbed on the steel surface by sharing of an electron pair of heteroatoms present in plant extract with orbital of iron forming covalent bond, leading to the positive value of ΔH_{ads} [14].

6 Conclusion

The Aqueous extract of Carum copticum seeds was found to be a good inhibitor for steel in 1 M Tartaric acid solution with inhibition efficiency reaching upto 63.64% at room temperature. The rate of corrosion of steel in 1 M Tartaric acid is observed as a function of the concentration of AECCS under experimental conditions. This rate is decreased as the concentration of AECCS is increased. The inhibition efficiency decreases with increase in temperature. The Aqueous extract of Carum copticum seeds is observed as a good, green, eco-friendly and cheaper corrosion inhibitor for steel in 1 M Tartaric acid solution.

7 Acknowledgement

The authors are thankful to the Head of Chemistry Department and Principal, Government College, Kota for providing necessary laboratory facilities.

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