Research Journal of Chemical Sciences ISSN 2231-606X
Vol. **2(9),** 37-41, Sept. **(2012)** *Res.J.Chem.Sci.*

The Effects of *Inula viscosa* Extract on Corrosion of Copper in NaOH Solution

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Available online at: www.isca.in
Received 1st June 2012, revised 7th June 2012, accepted 10th June 2012

Abstract

The effect of Inula viscosa extracts on the corrosion of copper in 1M NaOH solution was studied using weight loss method at various temperatures varying from 298 to 328 K. Experimental data revealed that Inula viscosa extract acted as an inhibitor in the alkaline environment. It was found that the inhibition efficiency increased with an increase in Inula viscosa extract concentration. Adsorption enthalpies were determined and discussed. Effect of temperature was also investigated and activation parameters were evaluated.

Keywords: *Inula viscosa,* weight loss, inhibition efficiency, copper.

Introduction

Copper has been one of preferred metals in industry owing to its excellent electrical and thermal conductivities, good mechanical workability, and its relatively noble properties[1]. In spite of the fact that copper is a relatively noble metal, it reacts easily in oxygen containing electrolytes. However, wide industrial application of copper has been based on its corrosion stability, which is the result of formation of an oxide/hydroxide layer on the metal surface. The oxide layer has, in general, a duplex structure made up of an inner Cu_2O layer followed by CuO and then a $Cu(OH)_2$ layer depending on the electrode potential [1]. Thin passivity layer formed on copper in neutral and alkaline solution has attracted considerable interest particularly in the corrosion catalysis and double layer structure research[2].

Some of these corrosion inhibitors are however, toxic to the environment. This has prompted the search for green corrosion inhibitors that are non-toxic and eco-friendly for metals and alloys in acidic and alkaline solutions[3]. These green corrosion inhibitors have been found to have centre for π-electrons and functional groups (such as –C = C-, -OR, -OH, $-NR_2$, $-NH_2$ and –SR) which provide electrons that facilitate the adsorption of the inhibitor on the metal surface.

Research on the use of plant extracts as corrosion inhibitors for metals/alloys in acid or alkaline media has therefore been intensified[3-10]. This is because plants are rich sources of naturally occurring chemical compounds that are environmentally acceptable, cheap and readily available.

Inula viscosa is a perennial herbaceous plant that profusely colonizes sub nitrophile and sub-saline soils in abandoned and plowed fields in the Mediterranean region. It exhibits simple alternate leaves, covered with glands secreting a sticky substance, and bright yellow flowers that bloom between August and November. This species is used topically in folk medicine as an anti-scabies and anti-inflammatory agent, and to promote wound healing[11-12]. Various compounds have been described that exhibit antioxidant such as Resveratrol, 1,3-dicaffeoylquinic acid[13].

The aim of the present work is to study the inhibition of copper surface by addition of *Inula viscosa* extract as inhibitor in NaOH solution by using weight loss technique.

Material and Methods

The weight loss measurements were carried out in a test tube placed in a thermostat water bath. The solution volume was 10 mL. The used copper coupons had a rectangular form (length = 1 cm, width = 1 cm, thickness = 0.03 cm). Prior to all measurements, the coupons were first polished successively with metallographic emery paper of increasing fineness up to1200 grits. The coupons was then washed with doubly distilled water, degreased with acetone, washed using doubly distilled water again and finally, dried with paper tissue at room temperature.

Inhibitor material: A Stock solution of the inhibitor material was prepared by refluxing 12.5 g of dry *Inula viscosa* powder with 250 mL of 1M NaOH for 3 hours. The refluxed solution was allowed to stand overnight and filtered through ordinary filter paper. From this solution, different concentrations of inhibitor solutions ranging from 0.1 to 0.7% were diluted.

Weight loss method: Pre-weighed copper specimens (in triplicate) were suspended for 1 hour in 1M NaOH with and without the inhibitor in different volume ranging from 1 to 7 mL of extract. After the specified time the coupons were removed from test solution, thoroughly washed with acetone solution and de-ionised water, dried well and then reweighed.

Results and Discussion

The plot of weight loss (mg) of copper coupon versus inhibitor volume for 60 min immersion period at different temperatures is shown in figure-1. Weight loss as a function of inhibitor volumes decreased gradually. This indicates that *Inula viscosa* extract inhibits the corrosion of copper in 1M NaOH solution. The values of percentage inhibitor efficiency (%I) for various concentrations of the inhibitor was determined for 1hr immersion periods by using the following equation:

$$\%I = [Wu - Wb/Wu] \times 100$$

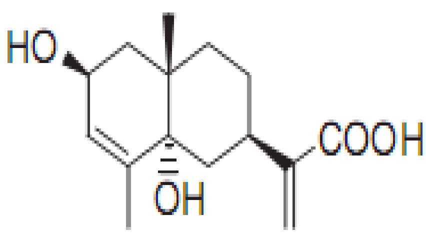
Where *W*u and *W*b are the uninhibited and inhibited weight losses, respectively. Assuming a direct relationship between inhibition efficiency (%I) and surface coverage (θ) for different inhibitor concentrations, the degree of surface coverage (θ) was calculated by using the following relationship:

$$\theta = \%I/100$$

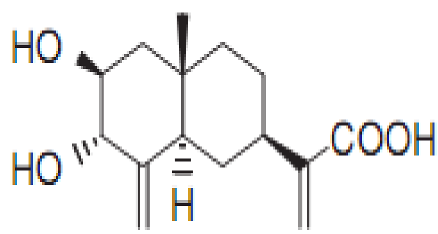
Table-1 collects the percentage inhibition efficiency for 60 min immersion periods at 25, 35, 45 and 55°C. The percentage inhibition efficiency values, as presented in table-1 for triplicate copper specimens. As seen in table-1, the percentage inhibition efficiency values increase with increasing extract concentration, but decrease with increasing temperature. The highest inhibition efficiency of 86.49% was obtained at 7mL of extract at 25°C. This result suggests that increase in extract concentration increases the number of inhibitor molecules adsorbed onto copper surface and reduces the surface area that is available for the direct base attack on the metal surface. The inhibitive effect of *Inula viscosa* is ascribed to the presence of organic compounds in the extract. *Inula viscosa* is rich in several organic compounds of high molecular weight with heteroatom and π centers in their molecular structures. These include 3-O-methylquercetin, 3,3′-di-O-methylquercetin, viscic acid, ilicic acid, resveratrol, cynaric acid 1,3-dicaffeoylquinic acid, 2,5-dihydroxyisocostic acid, 2,3-dihydroxycostic acid, isocostic acid, carabrone, tomentosin and hispidulin[14-15].

Table -1
Inhibition efficiency of *Inula viscosa* extract on copper in 1M NaOH for 60 min immersion period at different temperatures

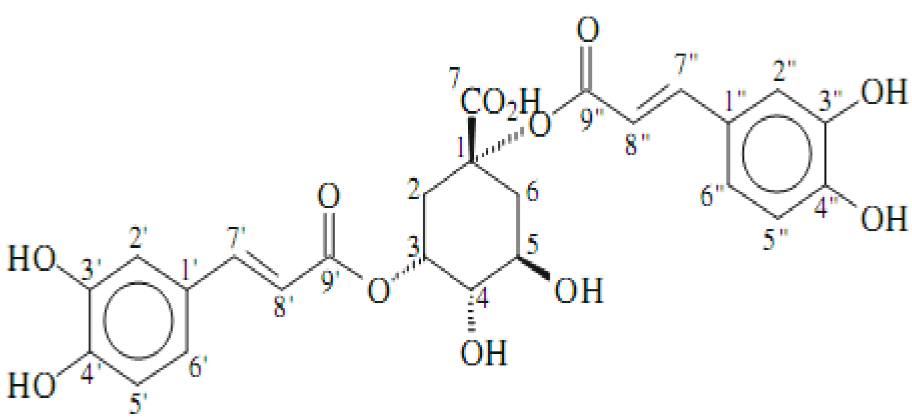
$V_{Extract}$	%I at 25 °C	%I at 35 °C	%I at 45 °C	%I at 55 °C
1	55.00	46.30	33.00	18.90
2	64.00	58.00	46.72	28.67
3	74.00	71.24	56.96	41.95
5	83.17	79.06	74.02	60.84
7	86.49	82.59	78.74	72.73



2,5-dihydroxy-isocostic acid



2,3-dihydroxycostic acid



1,3-dicaffeoylquinic acid

The inhibition effect of *Inula viscosa* may be due to the presence of these organic compounds in the extract. Since *Inula viscosa* contains several compounds, synergistic and antagonistic effects may play an important role on the inhibition efficiency of *Inula viscosa* as an inhibitor. Organic compounds having centers for π electrons and functional groups of O have been reported as corrosion inhibitors for copper in basic solutions[16]. The adsorption of these compounds on copper surface reduces the surface area that is available for the attack of the aggressive ion from the basic solution. As seen in figure-1, the weight loses decrease with increase in extract concentration due to higher degree of surface coverage, θ as a result of enhanced inhibitor adsorption. Similar view has been reported previously[5-8]. Also, figure-2 confirms that the inhibition is due to the adsorption of the active organic compounds onto metal surface. This is because a straight line is obtained when C/θ is plotted against C and the linear correlation coefficient of the fitted data is close to 1, indicating that the adsorption of the inhibitor molecules obey the Langmuir's adsorption isotherm expressed as[9].

$$C/\theta = C + 1/K$$

Where C is the inhibitor concentration and K the equilibrium constant for the adsorption/desorption process of the inhibitor molecules on the metal surface.

The effect of increase in solution temperature from 25 to 55 ºC on the inhibitor efficiency is summarized in table-1. An increased in temperature with produce a decrease in the inhibitor efficiency and this suggest that the process of adsorption of the inhibitor molecules is physical in nature. The apparent activation energy, Ea of the corrosion reaction was calculated by using the Arrhenius equation.

$$\mathrm{Log}(R_{Corr1}/R_{Corr2}) = E_a/2.303R(1/T_1-1/T_2)$$

Where R_{Corr1} and R_{Corr2} are corrosion rates at temperature T_1 and T_2, respectively. The corrosion rate (R_{Corr}, mg cm^{-2} h^{-1}) over the exposure time were calculated as follows [17-19].

$$\Delta W = (W_1-W_2)/A$$
$$R_{Corr} = \Delta W/ t$$

Where, W_1 is the original weight (mg) of the copper specimen, W_2 the weight after immersion in the test electrolyte, A is the area in cm^2, and t is the time of exposure in h.

The heat of adsorption, Q_{ads} was calculated by using the following equation[19].

$$Q_{ads} = 2.303\,R\ [\log\ (\theta_2/1-\theta_2) - \log\ (\theta_1/1-\theta_1)]\ x\ (T_2T_1/T_2-T_1)$$

Where θ_1 and θ_2 are the values of surface coverage at temperatures T_1 and T_2.

Arrhenius plot of logarithmic of corrosion rate against the reciprocal of absolute temperature (1/T) is shown graphically in figure-4 at different concentration of inhibitor. The values of activation energy (E_a) and heat of adsorption (Q_{ads}) are presented in table-2. The observed increase in activation energy in the presence of inhibitor from 53.06 to 71.97kJ mol^{-1}, with attendant decrease in inhibition efficiency of the inhibitor as temperature increases, suggests physical adsorption of the inhibitor molecules on the copper surface. This is in accordance with the findings of other workers[11,19]. The negative values of the Q_{ads} of adsorption and the high values of the adsorption constant indicate a spontaneous adsorption of these inhibitors on copper. This means that the inhibitive action of these substances results from the physical adsorption of these molecules on the surface of copper.

Table-2
The activation energy (Ea) kJ/mol and Q_{ads}(kJ/mol) of the copper with and without inhibitions

(%v/v)	Ea (kJ/mol)	Q_{ads} (kJ/mol)
0	53.06	-
1	58.30	-37.98
2	61.19	-29.57
3	63.10	-32.35
5	63.47	-9.13
7	71.97	-22.54

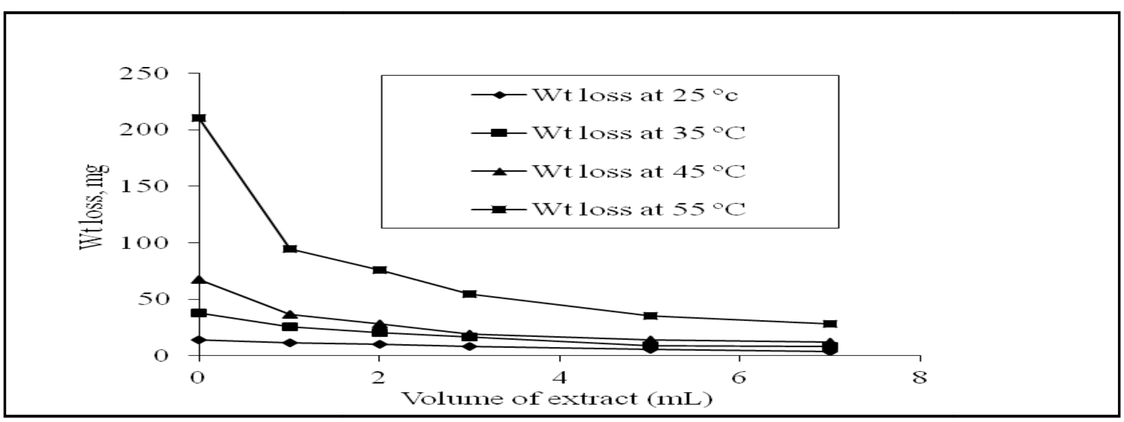


Figure-1
The plot of weight loss of copper coupon versus volume of *Inula viscosa* extract in 1M NaOH for 60 min. immersion period at different temperatures

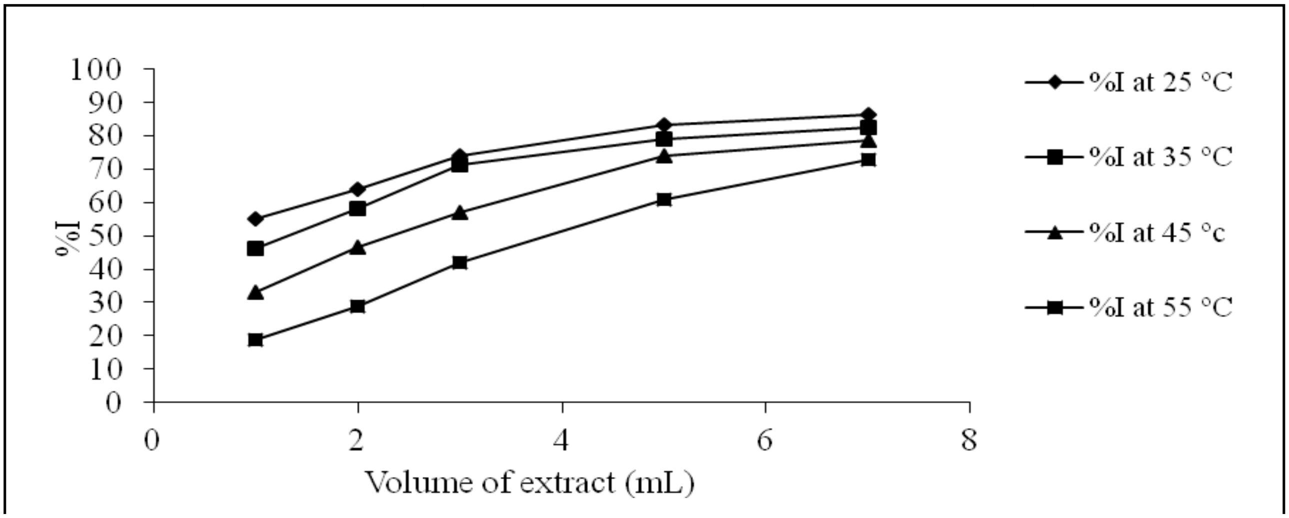


Figure-2
Inhibition efficiency of *Inula viscosa* extract on copper in 1M NaOH for 60 min immersion period at different temperatures

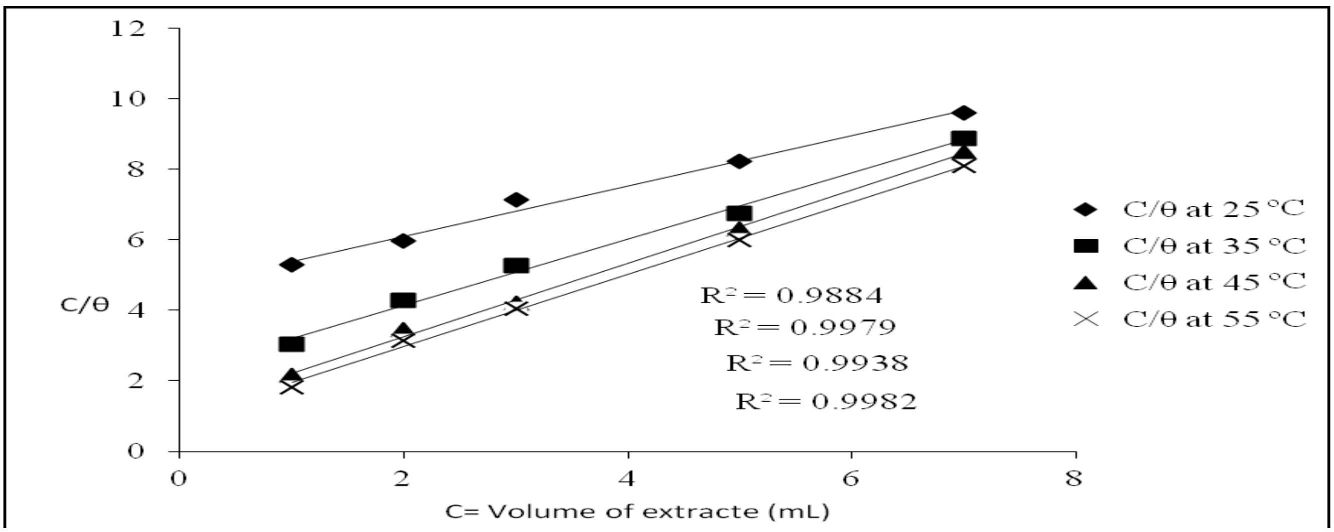


Figure-3
Langmuir isotherm for the adsorption on the copper surface of *Inula viscosa* extract at different temperature

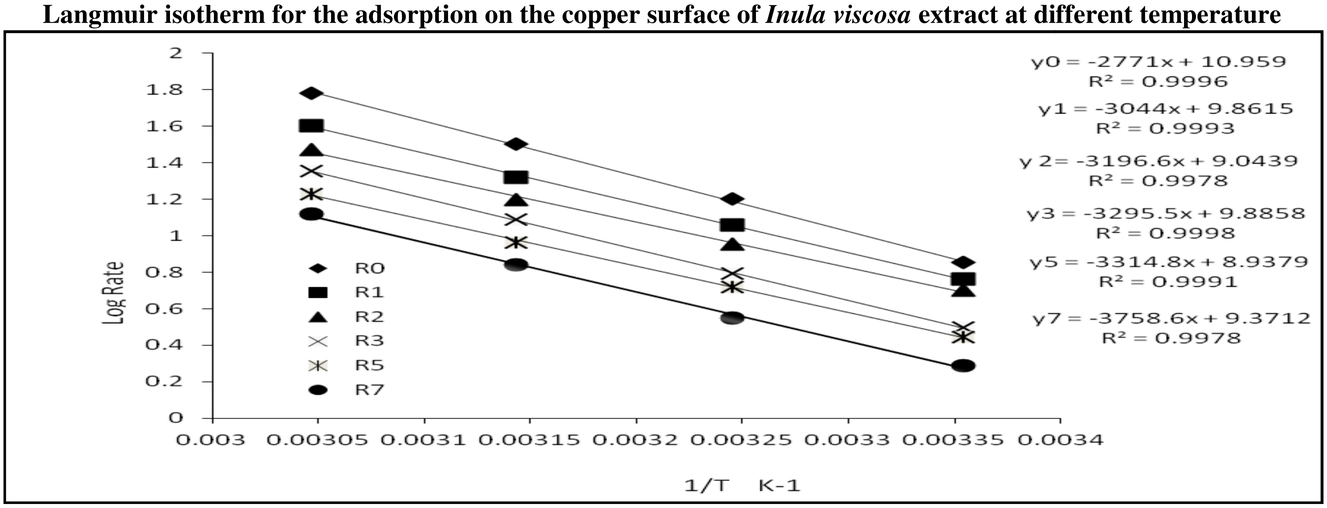


Figure-4
Arrhenius plot for copper dissolution in 1M NaOH in the absence and presence inhibitor

Conclusion

The extract of *Inula viscosa* inhibits the corrosion of copper in 1M NaOH solutions, with inhibition efficiency of 86.49% at 7mL of extract and the % inhibition efficiency decreased with increase in temperature. The adsorption of the inhibitor molecules was consistent with Langmuir adsorption isotherm.

Acknowledgment

The authors would like to thank the Yarmouk University for providing financial support. Special thanks are due to Prof. Dr. Mohammad Al-qudah.

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