The Effects of *Cassia Siamea* Lam. Root Extract on the Corrosion and Kinetics of Corrosion Process of Copper in Alkaline Solutions

A. I. ONEN*, B. T. NWUFO[§] and E. E. EBENSO

*Department of Chemistry, Adamawa State University, P.M.B 25, Mubi, Nigeria

[§]Department of Chemistry, University of Jos, Plateau State, Nigeria

Department of Chemistry, North West University (Mafikeng Campus)

Private Bag X2046, Mmabatho 2735, South Africa

alfredonen@yahoo.com

Received 1 March 2011; Accepted 22 April 2011

Abstract: The effect of *Cassia siamea* lam. (CSL) root extract as a corrosion inhibitor of copper in 0.50 M NaOH solutions was investigated using absorbance difference technique at 30 °C and 40 °C. CSL root extract inhibited the corrosion of copper in 0.50 M NaOH solutions and the inhibition efficiency (% IE) increased to a maximum of $78.3 \pm 2.3\%$ with increasing concentration of the extract but decreased with increasing temperature. The adsorption of CSL root extract on copper surface followed the Langmuir adsorption model with the average heat of adsorption, Q_{ads} and free energy of adsorption, ΔG_{ads} of -8.98 kJmol^{-1} and -8.70 kJmol^{-1} respectively. A kinetic treatment of the data revealed a first order kinetics with respect to copper in the presence and absence of the extract.

Keywords: Copper, Absorbance difference, Alkaline corrosion, Kinetic parameter

Introduction

Metals and alloys are often exposed to the action of acids and alkalis in industrial processes thereby prompting their deterioration¹. One of the most effective means of protecting metals and alloys surfaces from corrosion in acid and alkaline environments is the use of corrosion inhibitors². Corrosion inhibitors are usually added to the acid/alkaline solutions to reduce the metal loss. Recently, studies on the use of drugs have been reported by several researchers^{3,4}.

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 solutions⁵. These green corrosion inhibitors have been found to have centre for π -electrons and functional groups (such as $-\text{C}=\text{C}-$, $-\text{OR}$, $-\text{OH}$, $-\text{NR}_2$, $-\text{NH}_2$ and $-\text{SR}$) which provide electrons that facilitate the adsorption of the inhibitor on the metal/alloy surface.

Research on the use of plant extracts as corrosion inhibitors for metals/alloys in acid or alkaline media has therefore been intensified^{1,5-18}. This is because plants are rich sources of naturally occurring chemical compounds that are environmentally acceptable, cheap and readily available. For instance, *Cassia siamea* lam., CSL, is rich in several heterocyclic compounds^{7,13,14} of high molecular masses, with oxygen, nitrogen and sulphur atoms in their molecular structures.

Cassia siamea lam. leaf and stem extracts have recently been established as eco-friendly corrosion inhibitors of acid corrosion of mild steel⁸ and zinc¹⁴. Available literature shows that there is no reported work on the inhibition characteristics/effects of *Cassia siamea* lam. root extract on alkaline corrosion of copper. This paper reports the effects of *Cassia siamea* L. root extract on both the corrosion of copper and kinetics of corrosion process of copper in 0.50 M NaOH solution using absorbance difference technique.

Experimental

Copper sheets (98.7%) of 0.028 cm in thickness used for this study were obtained from Borno Wire and Nails Company Ltd in Maiduguri, Borno State of Nigeria. Each sheet was mechanically press cut into 4x3x0.028 cm rectangular specimens. The specimens were used as cut without further polishing to ensure reproducible surfaces¹. They were however, degreased in absolute ethanol, rinsed with double distilled water, dried in propanone and stored in air tight desiccators before using them for this study⁸. The average mass of the specimens used was 15.28 - 15.33 mg and the total surface area of the coupons exposed was 12.00 cm².

The NaOH was of analytical grade; used without further purification and 0.50 M of it was prepared and employed as the aggressive solution for the study. *Cassia siamea* Lam. roots were collected, washed, dried and pulverized. The extract was obtained from methanol (BDH), using soxhlet extractors and concentrated using a rotary evaporator. A concentration range of 10⁰ - 10¹ mgdm⁻³ (*i.e.* 1.0, 3.0, 5.0, 7.0 and 10.0 mgdm⁻³) of CSL root extract was prepared in 0.50 M NaOH and used as inhibitor test solutions.

Absorbance difference measurements

The procedure for absorbance difference measurements was similar to that reported earlier^{8,14} but at a wavelength¹⁵ of 457 nm and at 30 °C. The effect of temperature on the corrosion rate of copper specimens in 0.50 M NaOH at 40 °C was also investigated with different concentrations of (10⁰ - 10¹ mgdm⁻³) of the extract.

Results and Discussion

The plot of absorbance difference (Add) of copper specimen versus inhibitor concentration at 30 °C for 168 hours (7 days) is shown in Figure 1. The absorbance difference decreased gradually as the inhibitor concentration increased. This indicates that CSL root extract inhibits the alkaline corrosion of copper in 0.50 M NaOH solution. The values of percentage inhibition efficiency (% IE) were calculated for 24 hourly periods using the Equation (1)

$$\% \text{ IE} = (1 - A_1 / A_0) \times 100 \quad (1)$$

Where A₀ and A₁ are uninhibited and inhibited absorbance differences respectively¹. Since there is a direct relationship between percentage inhibition efficiency (% IE) and the degree of surface coverage (θ) for different inhibitor concentrations, the degree of surface coverage (θ) was determined using the expression

$$\theta = \% \text{ IE} / 100 \quad (2)$$

Figure 1. Plot of mean absorbance difference of copper specimen *versus* blank and inhibitor (CSL-root extract) concentration in 0.50 M NaOH solution for 168 hours at 30 °C and 40 °C

The percentage inhibition efficiency for 168 hours at 30 °C and 40 °C are shown in Table 1. The values of % IE as presented in Table 1 for triplicate copper specimens were precise to $\pm 2.3\%$ indicating good reproducibility. Table 1 and Figure 2 reveal that % IE values increase with increasing extract concentration but decrease with increasing temperature. The highest % IE of 78.3% was obtained at 10.0 mgdm⁻³ concentration at 30 °C.

Table 1. Summary of inhibition efficiency (% IE), corrosion rates, E_a and Q_{ads} of CSL-root extract on copper for 168 hours

Inhibitor conc. mgdm ⁻³	Inhibition efficiency, %		Corrosion Rate (Add) $\times 10^{-5}$		E_a , kJmol ⁻¹	Q_{ads} kJmol ⁻¹
	30 °C	40 °C	30 °C	40 °C		
Blank	-	-	11.10	11.60	3.48	-
1.0	63.7 $\pm$ 2.1	61.5 $\pm$ 0.9	3.04	3.41	9.06	-6.77
3.0	68.2 $\pm$ 1.2	66.4 $\pm$ 1.6	2.89	3.33	11.18	-7.13
5.0	72.2 $\pm$ 0.8	69.7 $\pm$ 2.2	2.70	3.09	10.64	-9.82
7.0	74.6 $\pm$ 1.8	71.8 $\pm$ 2.1	2.57	2.96	11.14	-8.00
10.0	78.3 $\pm$ 2.3	75.1 $\pm$ 1.8	2.28	2.74	14.49	-13.17
Average					11.30	-8.98

Figure 2. Plot of inhibition efficiency (% IE) *versus* inhibitor (CSL-root extract) concentration in 0.50 M NaOH solution for copper corrosion at 30 °C and 40 °C

The result suggests that increase in CSL root extract concentration increases the number of inhibitor molecules adsorbed on copper surface and reduces the surface area available for direct alkaline attack on the metal surface. This conforms to earlier findings of Abiola¹, Valek and Martinez¹⁶. The inhibitive characteristics of CSL root may be due to the presence of organic compounds in the extract. *Cassia siamea* lam. extract is rich in many organic compounds including alkaloids, anthraquinones, glycosides, phenols, saponins, steroids and tannins^{8,13,14} of high molecular masses with hetero-atoms and π -centres in their molecular structures.

The inhibitory effect of *Cassia siamea* L root extract is therefore linked to the presence of these organic compounds in the extract. The fact that CSL root contains several compounds, antagonistic and synergistic effects may play significant roles on the inhibition effectiveness of the extract as an inhibitor. Organic compounds containing functional groups with O, S or N and centre for π electrons or combination of both have been reported as corrosion inhibitor of copper¹⁶. The adsorption of these compounds on copper surface reduces the area that is available for the attack of the aggressive ion from the alkaline solution.

As observed in Figure 1, absorbance difference decrease with increase in root extract concentration due to higher degree of surface coverage, θ as a result of improved inhibitor adsorption. Similar views had previously been reported^{6,8,10,11,17}. Figure 3 also confirms that the inhibition process is due to adsorption of the active organic compounds on the 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 very close to 1. This indicates that the adsorption of CSL root extract molecules obeys the Langmuir adsorption model^{10,18} expressed as

$$C/\theta = C + 1/K \quad (3)$$

Where C is the inhibitor concentration and K is the equilibrium constant for the adsorption/desorption process of the inhibitor molecules on the metal surface. Values of adsorption parameters deduced from the plots are recorded on Table 2.

Figure 3. Langmuir adsorption model on copper surface of CSL-root extract in 0.50 M NaOH solution for 168 hours at 30 °C and 40 °C

The influence of the temperature increased (from 30 °C to 40 °C) on the inhibitor efficiency is presented in Table 1. Increase in temperature decreased the inhibitor effectiveness suggesting physisorption mechanism. The activation energy, E_a of the corrosion reaction was calculated using the rearranged Arrhenius Equation (4);

$$E_a = 2.303R \frac{T_1 T_2}{T_2 - T_1} \log \frac{\rho_2}{\rho_1} \quad (4)$$

Where ρ_1 and ρ_2 are corrosion rates at 30 °C and 40 °C respectively⁸. The heat of adsorption, Q_{ads} was determined using Equation (5);

$$Q_{ads} = 19.147 \left(\log \frac{\theta_2}{1-\theta_2} - \log \frac{\theta_1}{1-\theta_1} \right) \left(\frac{T_1 T_2}{T_2 - T_1} \right) \quad (5)$$

Where θ_1 and θ_2 are the values of surface coverage at 30 °C and 40 °C. The values of E_a and Q_{ads} are recorded in Table 1. The increase in E_a values in the presence of the inhibitor, with a decrease in % I_E of the inhibitor as the temperature increases further suggests physical adsorption of the inhibitor molecules on the copper surface. This is in agreement with the findings of other workers^{1,4,8,10,11,16,18}. The values of Q_{ads} are negative indicating that the adsorption process occurred exothermically. This observation further confirms physical adsorption of the inhibitor on the copper surface in NaOH solution. The relationship between the equilibrium constant, K , of adsorption and the free energy of adsorption, ΔG_{ads} , is given by the following expression^{3,16}:

$$\Delta G_{ads} = -2.303RT \log (55.5 K) \quad (6)$$

Values of free energy of adsorption calculated from equation (6) using K values obtained from the Langmuir adsorption are presented in Table 2. The values are negative and less than -40 kJmol⁻¹. This implies that the adsorption of the inhibitor on copper surface is spontaneous and confirms physical adsorption mechanism. This agrees with the findings of Valek and Martinez¹⁶.

Table 2. Values of Langmuir adsorption parameters and ΔG_{ads} at 30 °C and 40 °C

Temperature °C	Slope	log K	R ²	ΔG_{ads} , kJmol ⁻¹
30	1.2484	1.4817	0.9978	-8.60
40	1.2967	1.4661	0.9985	-8.79
Average				-8.70

As shown in Figure 4, the corrosion data fit the first - order reaction rate law as expressed in Equation (7)¹;

$$\log [A_i - \Delta A_t] = -kt/2.303 + \log A_i \quad (7)$$

Where A_i is the initial absorbance difference of copper specimen, ΔA_t is the absorbance difference of copper specimen at time t , $[A_i - \Delta A_t]$ is the residual absorbance of copper coupon at time t and k is the first - order rate constant. The linear plots obtained with correlation coefficients close to 1 confirm a first – order kinetics for the corrosion of copper in 0.50 M NaOH solution in the presence and absence of CSL root extract.

Figure 4. Plot of $\log [A_i - \Delta A_t]$ versus time, t (days) for copper specimens in 0.50 M NaOH solution with and without CSL-root extract at 30 °C

The anodic reaction order with respect to copper is also reflected by Figure 4. [*i.e.* anodic reaction Equation (8)];

This assertion has been reported earlier¹. It can be inferred from the result (Figure 4) that the inhibition of alkaline corrosion of copper by *Cassia siamea* Lam. root extract has no effect on the anodic reaction order. A similar plot was obtained for copper in NaOH solution (blank) and with the CSL root extract.

Conclusion

The results of this study shows that the extract of *Cassia siamea* Lam. root inhibits the corrosion of copper in 0.50M NaOH solutions, with the highest inhibition efficiency. (% IE) of 78.3±2.3% at 10.0 mgdm⁻³ extract concentration and % IE decreased with increase in temperature. The mechanism of adsorption of the inhibitor molecules on the surface of copper is physisorption and is consistent with Langmuir adsorption model. A first order kinetics relationship was obtained from the kinetic treatment of the absorbance difference data.

References

1. Abiola O K and James A O, *Corros Sci.*, 2010, **52**, 661-664.
2. Ebenso E E, Arslan T, Kandemirli F, Caner N and Love I, *Int J Quantum Chem.*, 2010, **110**, 1003-1018.
3. Eddy N O, Ibok U J, Ebenso E E, El Nemr A and El Ashry E S, *J Mol Model.*, 2009, **15**, 1085-1092.
4. Onen A I, *J Chem Soc Nig.*, 2007, **32(1)**, 227.
5. Oguzie E E, *Corros Sci.*, 2007, **49**, 1527-1539.
6. Onen A I, *Nig J Appl Sci.*, 2004, **22**, 174.
7. Okafor P C, Ebenso E E, Ibok U J, Ekpe U J and Ikpi M E, *Trans SAET*, 2003, **38**, 91
8. Orubite-Okorosaye K and Oforka N C, *J Appl Sci Environ.*, 2004, **8(1)**, 57-61.
9. Abdel-Gaber A M, Khamis E, Abo-ElDahab H and Adeel S h, *Mater Chem Phys.*, 2008, **109**, 297-305.
10. Abiola O K and Otaigbe J O E, *Corros Sci.*, 2009, **51**, 2790-2793.
11. Abiola O K, Otaigbe J O E and Kio O J, *Corros Sci.*, 2009, **51**, 1879.
12. Orubite K O and Oforka N C, *Mater Lett.*, 2004, **58(11)**, 1768.
13. Lu T S, Yi Y H, Yuan H Y, Zhang Z G and Liu W, *Medscape*, 2003, **38(2)**, 113-315.
14. Onen A I, Maitera O N, Joseph J and Ebenso E E, *Int J Electrochem Sci.*, **6**, 2884-2897.
15. Obot I B, Obi-Egbedi N O and Umoren S A, *Int J Electrochem Sci.*, 2009, **4**, 863
16. Valek L and Martinez S, *Mater Lett.*, 2007, **61**, 148-151.
17. Abiola O K and Oforka N C, *Scientia Africana*, 2003, **2**, 82.
18. Okafor P C, Ikpi M E, Uwah I E, Ebenso E E, Ekpe U J and Umoren S A, *Corros Sci.*, 2008, **50(8)**, 2310-2317.