Inhibition of Copper Corrosion by Flavonoids in Nitric Acid

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Abstract: A study has been made to investigate the effect of some substituted flavonoids on copper dissolution in 2.0 M HNO_3 for 4.0 hours at different temperatures by the weight loss method. Percentage of inhibition increases as concentration of the flavonoids increases and reaches a maximum value, due to the formation of a monolayer film on the surface of the metal. 92% Inhibition was observed in some of these flavonoids. As temperature increases, percentage of inhibition decreases. Energy of activations were deduced and discussed.

Keyword: Copper; Corrosion, Flavonoids, Inhibition, Quercetin-3,3'-dimethylether.

Introduction

Copper and its alloys are widely used materials for their excellent electrical and thermal conductivities in many applications such as electronics¹ and recently in the manufacture of integrated circuits²⁻⁴. Copper is relatively noble metal, requiring strong oxidants for its corrosion or dissolution. The chemical dissolution and electrolytic plating are the main processes used in the fabrication of electronic devices. The most widely used corrosive solution contains nitric acid, so this medium has induced a great deal of research on copper corrosion⁵⁻¹⁰. In order to study the corrosion of metals, several techniques have been applied. The use of chemical inhibitors is one of the most practical methods for the protection against corrosion in acidic media. Most of the excellent acid inhibitors are organic compounds containing nitrogen¹¹⁻¹³, oxygen¹⁴⁻¹⁷, phosphorus¹⁸ and sulphur¹⁹⁻²². Studies of the relation between adsorption and corrosion inhibition are of considerable importance.

Flavonoids are water soluble polyphenolic molecules containing 15 carbon atoms (Scheme 1). Flavonoids are widely disbursed throughout plants and give the flowers and fruits of many plants their vibrant colors. Flavonoids have antioxidant activity, anti-allergic, anti-cancer, anti-inflammatory and anti-viral²³.

In this study, some flavonoids compounds such as apigenin (**1**), luteolin-3'-methyl ether (**2**), quercetin-3,3'-dimethylether (**3**) and jeceidine (**4**) (Scheme 1) were used to study the corrosion behaviour of copper in 2.0 M HNO₃ using the weight loss method.

Scheme 1. Chemical structures of the tested flavonoids used for inhibition of copper corrosion in nitric acid.

Chemicals

Nitric acid solutions were prepared from the RP Normapur grade HNO₃ (65% Merck) in distilled water. Copper sheet (99.9% Prolabo Chemicals or 99.98% Aldrich Chemicals) was cut as coupons of total surface area of 2.21 cm². Compounds **1-4** were isolated from *Varthemia iphionoides*. The compounds exhibited the following characteristics.

Apigenin (**1**)

IR (KBr) cm⁻¹: 3295, 2910, 1650, 1603, 1585, 1493, 1350, 1242, 1180, EIMS *m/z* (%): 270 [M⁺] (C₁₅H₁₀O₅) (100), 242 (9), 153 (28), 121 (23), 69 (31), 55 (18). UV λ_{max} (MeOH) nm = 337 (band I), 270 (band II), +NaOMe = 401 (band I), 285 (band II), 325 (OH - 7). +AlCl₃, 345 (Band Ib), 380 (Band Ia), 275 (band IIb), 301 (Band IIa); +HCl, 338 (Band Ib), 380 (Band Ia), 278 (band IIb), 300 (Band IIa). ¹H NMR (DMSO - d₆) δ ppm = 6.15 (1H, d, J = 1.7 Hz, H-6), 6.43 (1H, d, J = 1.7 Hz, H-8), 6.70 (1H, s, H-3), 6.75 (2H, d, J = 8.7 Hz, H - 3', 5'), 7.85 (2H, d, J = 8.7 Hz, H - 2', 6'), 10.55 (2H, broad, OH-7,4'), 12.90 (1H, s, OH - 5). ¹³C NMR (DMSO - d₆) δ ppm = 94.3 (C-8), 99.3 (C-6), 103.3 (C-3), 104.2 (C-10), 116.4 (C - 3', 5'), 121.7 (C - 1'), 129.0 (C - 2', 6'), 157.8 (C-9), 161.7 (C - 4'), 161.9 (C-5), 164.2 (C-2), 164.6 (C-7), 182.2 (C-4).

Luteolin-3'-methyl ether (**2**)

IR (KBr) ν_{max} (cm⁻¹): 3360, 3100, 1652, 1625, 1564, 1515, 1442, 1355, 1301, 1215, 1166, 1033. EIMS *m/z* (%): 300 [M⁺] (C₁₆H₁₂O₆) (25), 257(5), 229(5), 153(10), 133(8) 105 (5), 69(8). UV λ_{max} (MeOH) nm: 347 (band I), 270 (band II); + NaOMe, 405 (band I), 325, 270 (band II); + AlCl₃, 360 (band I), 260 (band II); + HCl, 350 (band I) 260 (band II). ¹H NMR (DMSO -d₆) δ ppm: 3.85 (3H, s, 3'-OMe), 6.15 (1H, br s, H-6), 6.45(1H, br s, H-8), 6.83 (1H, s, H-3), 6.89 (1H,d, J = 8.7Hz, H-5'), 7.50 (2H, br s, H-2',6'), 10.03 (1H, broad, OH), 10.68 (1H, broad, OH), 12.94 (1H.s, 5-OH). ¹³C NMR (DMSO -d₆) δ ppm: 56.4 (3'-OMe), 94.5 (C-8), 99.3 (C-6), 103.7 (C-3), 104.2 (C-10), 110.6 (C-2'), 116.2 (C-5'), 120.6 (C-6'), 122.0 (C-1'), 148.5 (C-3'), 151.2 (C-4'), 157.8 (C-9), 161.9 (C-5), 164.1 (C-2), 164.6 (C-7), 182.3 (C-4).

Quercetin-3,3'-dimethylether (3)

IR (KBr) $\nu_{\max}$ (cm⁻¹): 3165, 1650, 1610, 1590, 1510, 1370, 1310, 1220. EIMS m/z (%): 330 [M⁺] (C₁₇H₁₄O₇) (65), 315(45), 287(57), 269(10), 244(15), 217(8), 151 (18), 84(58), 66(72). UV $\lambda_{\max}$ (MeOH) nm: 357 (band I), 255 (band II); + NaOMe, 412 (band I), 270 (band II); + AlCl₃, 405 (Band Ia), 357 (band Ib) 303 (band IIa), 269 (band IIb); + HCl, 407 (band Ia), 364 (Band Ib), 303 (band IIa), 269 (Band IIb). ¹H NMR (DMSO d₆) δ ppm: 3.79(3H, s, 3'-OMe), 3.85(3H, s, 3-OMe), 6.19 (1H, d, J = 2Hz, H-6), 6.46 (1H, d, J = 2Hz, H-8), 6.95 (1H, d, J = 8.4Hz, H-5'), 7.56 (1H, dd, J = 2.1, 8.5Hz, H-6'), 7.63 (1H, d, J = 2Hz, H-2'), 12.66(1H, s, 5-OH). ¹³C NMR (DMSO -d₆) δ ppm: 55.7 (3'-OMe), 59.7 (3-OMe), 93.8 (C-8), 98.5 (C-6), 104.2 (C-10), 112.0 (C-6'), 115.6 (C-2'), 120.8 (C-5'), 122.2 (C-1'), 137.7 (C-3), 147.4 (C-3'), 149.7 (C-4'), 156.3 (C-9), 160.9 (C-2), 161.2 (C-5), 164.1 (C-7), 177.9 (C-4).

Jeceidine (4)

IR (KBr) $\nu_{\max}$ (cm⁻¹): 3360, 2950, 1656, 1602, 1556, 1511, 1486, 1297, 1261, 1182. EIMS m/z (%): 360 [M⁺] (C₁₈H₁₆O₈) (100), 345 (90), 317(70), 299(45), 274(25), 246(13), 167(32), 151 (50), 69(75). UV $\lambda_{\max}$ (MeOH) nm: 355 (band I), 275 (band II); + NaOMe, 415 (band I), 273 (band II); + AlCl₃, 367 (band I), 265 (band II); + HCl, 367 (band I) 265 (band II). ¹H NMR (DMSO - d₆) δ ppm: 3.72, 3.76, 3.82 (9H, 3OMe,s), 6.54 (1H, s, H-8), 6.92 (1H, d, J = 8.4Hz, H-5'), 7.53 (1H, d, J = 8.3 Hz, H-6'), 7.60 (1H, broad singlet, H-2'), 12.74 (1H,s, 5-OH). ¹³C NMR (DMSO - d₆) δ ppm: 56.2 (6-OCH₃), 60.2 (3-OCH₃), 60.5 (3'-OCH₃), 94.6 (C-8), 105.1 (C-10), 112.5 (C-2'), 116.1 (C-5'), 121.3 (C-1'), 122.7 (C-6'), 131.6 (C-6), 137.9 (C-3), 147.9 (C-3'), 150.3 (C-4'), 152.0 (C-9), 152.9 (C-5), 156.0 (C-2), 157.9 (C-7), 178.7 (C-4).

Experimental

The weight loss measurements were carried out in a test tube placed in a thermostat water bath. The solution volume was 5 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 to 1200 grits. The electrode was then washed with doubly distilled water, degreased with acetone, washed using doubly distilled water again and finally, dried with tissue paper at room temperature. The coupons were weighed and suspended in 5 mL of 2.0 M HNO₃ solution containing flavonoids derivatives at the desired concentrations for 4 h at 25 °C. At the end of the tests, the coupons were taken out, washed with distilled water, degreased with ethanol, washed again with distilled water, dried and then weighed using an analytic balance (precision: ± 0.1 mg).

Results and Discussion

The variation of copper weight loss (g) in the presence of varying concentration (1×10^{-4} – 5×10^{-7} M) of the different organic compounds (**1-4**) (Scheme 1) in 2.0 M HNO₃ for 4.0 h at 25 °C were collected in Table 1 and were plotted in Figure 1.

Table 1. Copper weight loss on the presence of varying concentration (M) of organic compounds (**1-4**) in 2.0 M HNO₃ for 4.0 h

Conc., M	1	2	3	4
1.0×10^{-4}	0.0182	0.0125	0.0090	0.0070
5.0×10^{-5}	0.0251	0.0163	0.0126	0.0089
1.0×10^{-5}	0.0436	0.0335	0.0176	0.0134
5.0×10^{-6}	0.0561	0.0394	0.0210	0.0159
1.0×10^{-6}	0.0721	0.0595	0.0268	0.0210
5.0×10^{-7}	0.0804	0.0662	0.0318	0.0243

According to Figure 2 the following observations could be deduced for the dissolution of copper metal in 2.0 M HNO₃ for 4.0 h.

- Drastic decrease in the weight loss of copper metal as the concentration of the organic compounds **1** and **2** increases, especially at low concentration.
- A slight decrease in the weight loss of copper metal as the concentration of the organic compounds **3** and **4** increases.
- Weight loss of copper metal reaches limiting value for all organic compounds **1-4**.

All additives appeared to acts as inhibitors over the concentration range studied. The percentage inhibitions (I) calculated from the weight loss (equation 1)²⁴ for all organic compounds (Table 2) are plotted in Figure 2.

$$L\% = \left(I - \frac{W_{t(w)}}{W_{t(w_0)}} \right) \times 100 \quad (1)$$

$$\theta = \left(1 - \frac{W_{t(w)}}{W_{t(w_0)}} \right) \quad (2)$$

Figure 1. Weight loss curves for copper in 2.0 M HNO₃ in the presence of different concentrations (M) of compounds (**1-4**) at 25 °C for 4.0 h.

Figure 2. Effect of organic compounds concentration on inhibition efficiency (%I) for corrosion of copper in 2.0 M HNO₃ after 4.0 h immersion at 25 °C

Where $W_{t(w_0)}$ and $W_{t(w)}$ are weight loss of copper metal without and with the presence of the organic compounds in 2.0M HNO₃ for 4.0 h.

Table 2. Inhibition efficiency (%I) of the different concentrations of compounds (**1- 4**) for the corrosion of copper in 2.0 M HNO₃ after 4.0 h immersion at 25 °C

Conc, M	% I			
	1	2	3	4
1.0×10^{-4}	78.3	85.1	89.3	91.6
5.0×10^{-5}	70.0	80.5	85.7	89.4
1.0×10^{-5}	47.6	60.0	79.0	84.0
5.0×10^{-6}	36.1	53.3	75.1	81.4
1.0×10^{-6}	13.8	29.0	68.3	75.2
5.0×10^{-7}	4.0	20.5	61.9	70.5

The inhibition effect of all organic compounds (**1-4**) increases with increasing the additive concentration and reach a limiting value. This limiting value is believed to be related to the formation of a monolayer film of the adsorbent on the active sites of the metal. Evidence to support this conclusion was obtained by plotting Langmuir adsorption isotherm²⁵. Figure 3 illustrates the plotting of $\log (\theta/1-\theta)$ versus $\log$ concentration for all compounds (equation 3). The resulting straight line relationships support the fact that the inhibition is due to adsorption of the organic compounds. By comparing the value of I at the limiting value and the corresponding inhibitor concentration, one can conclude that the relative strength of these organic compounds as inhibitors decreases in the following order **4>3>2>1**.

Figure 3. $\log (\theta/1-\theta)$ vs. $\log C$ curves for corrosion of copper in the presence of different concentrations of all flavonoids derivatives at 25 °C.

All substrates in Scheme 1 are substituted flavonoids. Thus one can correlate the inhibitory effect of these compounds with the substituents on the flavonoids. It is believed that compounds **1** adsorbed on the active sites of copper metal *via* the carbonyl and hydroxyl groups at position 4 and 5, respectively. Addition of methoxy group (OCH_3) at position 3, which is an electron donating group (compound **2**), enhances to some extent the adsorption process. Addition of another OCH_3 group at position 3 (compound **3**) and another OCH_3 group at position 6 enhances remarkably the adsorption process through increasing the %I to 91.6% for compound **4** when the concentration of compound **4** was 1×10^{-4} .

All flavonoids **1-4** have the same stem with different substituents of OCH_3 groups at different positions. The %I of compounds **3** and **4** are very high even at low concentrations, indicating that both compounds adsorbed strongly at the surface of copper metal due to a decrease in steric effect.

Upon increasing temperature from 25 °C to 55 °C the %I decreases for all compounds, with the same order obtained at 25 °C in 2.0 M HNO_3 for 4 hour at 1×10^{-4} M of the different organic compounds (Table 3) as shown in Figure 4, indicating that the corrosion inhibition takes place by adsorption of the inhibitors at the electrode solution interface²⁶.

Table 3. Inhibition efficiency (%I) at 1×10^{-4} M of compounds (**1- 4**) for the corrosion of copper in 2.0 M HNO_3 after 4.0 hour immersion at different temperature

T, °C	Inhibition at 1×10^{-4} M			
	1	2	3	4
25	78.3	85.1	89.3	91.6
35	44.4	51.2	57.4	58.5
45	18.8	21.1	34.9	38.5
55	0.5	2.2	17.5	19.6

Figure 4. Inhibition efficiency (%I) at 1×10^{-4} M of compounds (1- 4) for corrosion of copper in 2.0 M HNO_3 after 4.0 hour immersion at 25, 35, 45 and 55 °C

Energy of activation (E_a) was obtained by plotting log rate of corrosion ($\text{mg}/\text{cm}^2 \cdot \text{s}$) versus $1/T$ (Table 4) and shown in Figure 5. E_a was found to be 114.1, 123.8, 127.3 and 132.9 kJ/mol for compounds 1 to 4, respectively. And for copper in 2.0 M HNO_3 without the presence of the inhibitor is equal 73.4 kJ/mol, which in accordance with literature value²⁷. This result is in accordance with the strength of adsorption on the surface of copper metal²⁸.

$$\Delta W = \frac{W_1 - W_2}{A} \quad (4)$$

$$R_{\text{Corr}} = \frac{\Delta W}{t} \quad (5)$$

Where, R_{corr} is the corrosion rate ($\text{mg}/\text{cm}^2 \cdot \text{s}$), W_1 is the initial weight of the specimen (mg), W_2 the specimen weight (mg) after the immersion period, 't' is the immersion time (s) and A is area of the specimen (cm^2).

Table 4. Variation of log rate without and with the presence of inhibitors *verses* reciprocal of temperature

$1/T, 10^{-3}$	log rate				
	Copper	1	2	3	4
3.350	-2.73	-3.39	-3.55	-3.69	-3.8
3.243	-2.35	-2.61	-2.66	-2.72	-2.73
3.143	-1.95	-2.04	-2.05	-2.14	-2.16
3.047	-1.58	-1.58	-1.59	-1.66	-1.67

Figure 5. Arrhenius plots of copper in 2 M HNO_3 with and without different compounds (1-4)

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References

1. Oteino-Alergo V, Huynh N, Notoya T, Bottle S E and Schwcinsberg D P, *Corros Sci.*, 1999, **41**, 685.
2. Tsai H Y, Sun S C and Wang S J, *J Electrochem Soc.*, 2000, **147**, 2766.
3. Krishnamoorthy A, Chanda K, Murarka S P, Pamanath G and Ryan J G, *Appl Phys Lett.*, 2001, **78**, 2467-2469.
4. Ho C E, Chen W T and Kao C R, *J Electron Mater.*, 2001, **30**, 379.
5. Evans U R, *Trans Farad Soc.*, 1944, **40**, 120.
6. Krosilshchikov A I and Dedova I V, *J Gen Chem U.S.S.R.*, 1946, **16**, 537.
7. Komuro Y, *J Chem Soc Jpn.*, 1954, **75**, 255.
8. Travincek E A and Weber J H, *J Phys Chem.*, 1961, **65**, 235.
9. Smol'yaninov I S, Voronezhsk Izv, *Gos Ped Inst.*, 1964, **47**, 34.
10. Rasheed Arain A and Shams El Din A M, *Thermochim Acta*, 1985, **89**, 171.
11. Abd-El-Nabey B A, Khamis E, Ramadan M Sh and El-Gindy A, *Corrosion*, 1996, **52**, 671.
12. Quraishi M A and Jamal D, *Corrosion*, 2000, **56**, 156.
13. Lagrene'e M, Memaru B, Chaibi N, Traisnel M, Vezin H and Bentiss F, *Corros Sci.*, 2001, **43**, 951.
14. Abd EI-Rehim S S, Ibrahim M and Khaled K F, *J Appl Electrochem.*, 1999, **29**, 593.
15. Bentiss F, Traisnel M, Gengembre L and Lagrene'e M, *Appl Surf Sci.*, 1999, **152**, 237-249.
16. Hosseini M G, Mertens S F L, Ghorbani M and Arshadi M R, *Mater Chem Phys.*, 2003, **78**, 800.
17. Migahed M, Mohamed H M and Al-Sabagh A M, *Mater Chem Phys.*, 2003, **80**, 169.
18. Khamis E, El-Ashry E S H and Ibrahim A K, *Br Corros J.*, 2000, **35**, 150.
19. Quraishi M A and Sharma H K, *Mater Chem Phys.*, 2002, **78**, 18-21.
20. Popova A, Sokolova E, Raicheva S and Christov M, *Corros Sci.*, 2003, **45**, 33-58.
21. Quaraishi M A and Rawat J, *Mater Chem Phys.*, 2002, **77**, 43.
22. El Azhar M, Memari B, Traisnel M, Bentiss F and Lagrene'e M, *Corros Sci.*, 2001, **43**, 2229.
23. Agrawal P K, *Carbon-13NMR of flavonoids*. Elsevier science publishers, Amsterdam, 1989.
24. Ahamad I and Quraishi M A, *Corros Sci.*, 2009, **51(9)**, 2006-2013
25. Abiola O K, Oforka N C, Ebenso E E and Nwinuka N M, *Anti-Corrosion Methods and Materials*, 2007, **54(4)**, 219-224.
26. Rudresh H B and Mayanna S M, *Surf Coating Technol.*, 1977, **6**, 139.
27. Fouda A S, Abd El-Aal A and Kandil A B, *Desalination*, 2006, **201**, 216-233.
28. Fouda A S, Gouda M M and El-Rahaman S I A, *Bull Korean Chem Soc.*, 2000, **21(11)**, 1085-1089.