

**EFFECT OF SOME ANALYTICAL ORGANIC INDICATORS
ON THE CORROSION OF NICKEL IN
CARBONATE SOLUTION**

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ABSTRACT

The effect of some analytical organic indicators e.g. methyl red, methyl orange and methyl violet on the corrosion of nickel electrode in 0.1M K_2CO_3 was studied using galvanostatic and potentiodynamic anodic polarization techniques. The percentage inhibition efficiency was found to increase with increasing concentration of these compounds. The inhibitive action of these compounds is due to adsorption of these compounds on the nickel surface, making a barrier to mass and charge transfer, following Freundlich isotherm. The inhibition efficiency decreases in the order: methyl red > methyl orange > methyl violet .It was found that, the addition of the chloride, bromide, iodide and thiosulfate ions accelerates the pitting corrosion of nickel in 0.1M K_2CO_3 solutions by shifting the pitting potential to more negative direction. The addition of these analytical organic compounds protects the nickel against pitting corrosion in bromide containing solution.

Keywords: methyl red, methyl orange, methyl violet, nickel, K_2CO_3 , pitting corrosion.

1-INTRODUCTION

Nickel and nickel alloys are important materials for the design vessels in different processes industry. Nickel electrode is also used in different energy-producing cell in which aqueous or non aqueous solutions are used as electrolytes. Nickel and its alloys exhibit excellent corrosion resistance in aqueous aggressive environments, which are

attributed to the ability of nickel to form a stable passive film on its surface [Singh & Banerjee (1986)]. Among alternative corrosion inhibitors, organic compounds containing polar functions with nitrogen, oxygen, sulfur atoms in conjugated system have been reported as effective inhibitors of nickel corrosion [Abdallah & El-Etre (2003); Aksut & Bilgic (1992); Frignani et al., (1998); EL-Etre et al., (2005) and Lallemand et al., (2007)]. Their inhibitive action is connected with several factors including the structure and charge distribution of the molecule, the number and types of adsorption sites and the nature of interaction between the molecule and the metal surface [Ebenso (2002)].

A recent contribution involves the study of organic indicators, whose molecules possess certain desirable characteristics as potential inhibitors in metal corrosive systems [Oguzie (2005) and Oguzie et al., (2004)].

The aim of this work is to study the effect of some organic analytical indicators as corrosion inhibitors of nickel in 0.1M K_2CO_3 solution using galvanostatic polarization measurements. Moreover, the ability of these compounds to provide a protection against pitting corrosion was studied using potentiodynamic anodic polarization technique.

2-EXPERIMENTAL

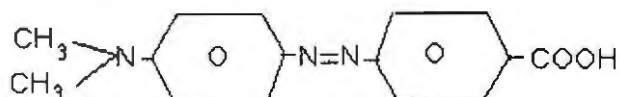
Pure nickel electrode (99.99%) was used in the present work. For galvanostatic experiments, a cylindrical rod was embedded in araldite leaving an exposed bottom area of (0.196cm²), and used as working electrode. This working electrode was polished with different grades of emery papers, degreased with acetone and rinsed with distilled water, before its immersion in the test solution. Galvanostatic and potentiodynamic anodic polarization techniques were carried out using a PS remote potentiostat with PS6 software for calculation of corrosion parameters. A three compartment cell with a saturated calomel reference electrode (SCE) and a platinum foil auxiliary electrode was used. The inhibition efficiency (IE) and surface coverage (θ) were calculated using the following equations:

$$\%IE = [(I - I_i)/I] \times 100 \quad (1)$$

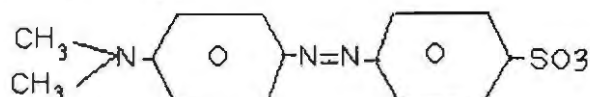
$$\theta = [(I - I_i)/I] \quad (2)$$

where I and I_i are the corrosion rates in free and inhibited alkaline solutions respectively. All chemicals used for preparing the test solution were of analytical grade and the experiments were carried out at room temperature, $25 \pm 1^\circ\text{C}$. The chemical structures of these organic additives are:

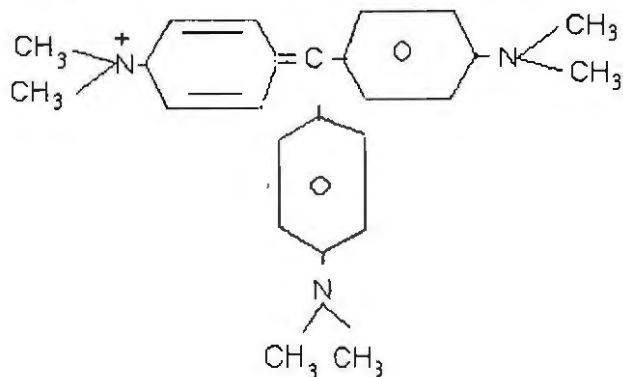
Compound 1: methyl red.



Compound 2: methyl orange.



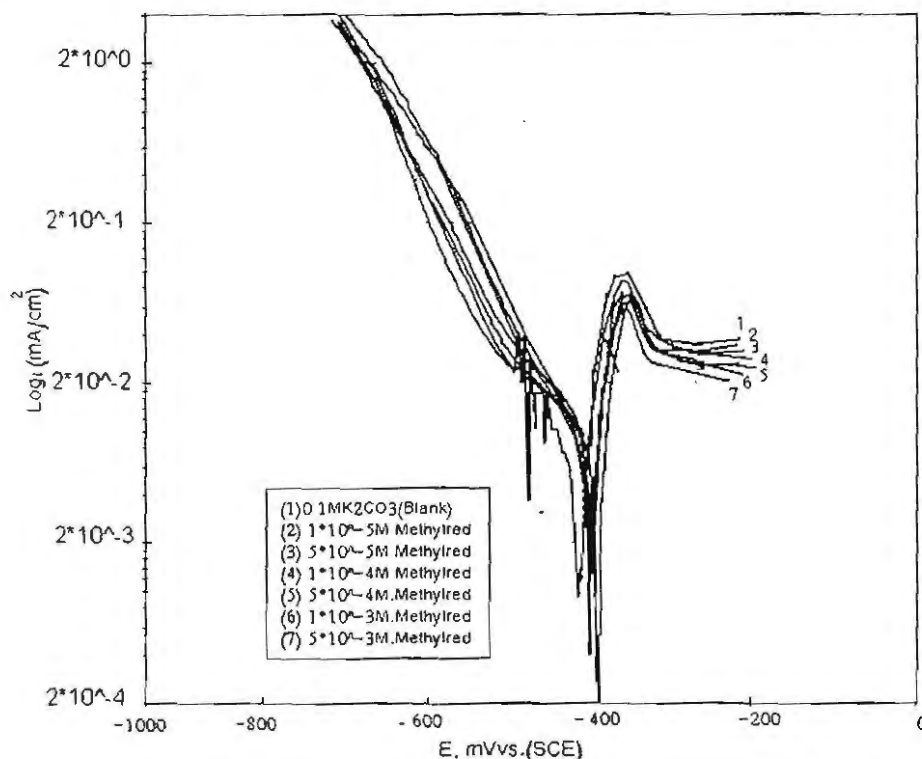
Compound 3: methyl violet or crystal violet, or gentiana violet.



3-RESULTS AND DISCUSSION

3.1. Galvanostatic polarization studies:

The effect of addition of some organic additives (methyl red, methyl orange and methyl violet) on the anodic and cathodic polarization curves for nickel in $0.1\text{M K}_2\text{CO}_3$ solution at 25°C was studied. The effect of increased concentration of methyl red is represented in Fig (1) as an example. However, similar curves were obtained for other two compounds (not shown). From Fig (1), one can observe at first, that there is a transition region in which the potential increases (anodic polarization) or decrease (cathodic polarization) slowly with current density followed by a rapid linear build up of potential with current density (Tafel region).



Figure(1):Galvanostatic polarization curves for nickel in 0.1M K₂CO₃ in the absence and presence of different concentrations of methylred

Table (1) shows the effect of additives concentration on the corrosion kinetic parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), cathodic and anodic Tafel slopes (β_c & β_a), surface coverage (θ) and inhibition efficiency (%IE) obtained from galvanostatic polarization measurements at 25°C. The corrosion current density (I_{corr}) and corrosion potential (E_{corr}) were determined by the interaction of the extrapolating anodic and cathodic Tafel lines, (%IE) was calculated from eq. (1) and β_c and β_a are the slope of the cathodic and anodic Tafel lines, respectively.

Inspection of Table (1) reveals that, the increasing in the concentration of the additives show the following:

- (a) The Tafel lines are shifted to more positive and negative potential for anodic and cathodic processes, respectively, relative to the blank curve. This means that these compounds influence both cathodic and anodic processes. However, the data suggested that these compounds act as mainly as mixed type inhibitors, but the cathode is more polarized when an external current was applied $\beta_c > \beta_a$.

- (b) E_{corr} changed slightly and the values of I_{corr} decrease indicating the inhibiting effect of these compounds.
- (c) The inhibition efficiencies of the three tested compounds by the galvanostatic polarization method decreases in the following order:
methyl red > methyl orange > methyl violet

3.2. Adsorption isotherm:

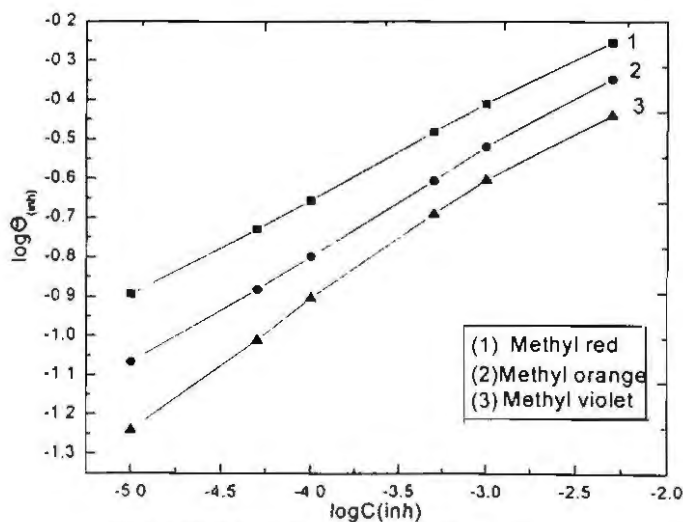
The experimental data for the tested inhibitors have been applied to different adsorption isotherm equations. The best correlation fits the Freundlich adsorption isotherm [Damaskin et al., (1971)] which is given as:

$$\theta = K C^n \quad (3)$$

or alternatively, by

$$\log \theta = \log k + n \log C \quad (4)$$

where k and C represent the equilibrium constant of adsorption process and additive concentration respectively.



Figure(2): Freundlich adsorption isotherm.
1)methyl red 2)methyl orange 3)methyl violet

Fig (2) represents the Freundlich adsorption plots for the compound studied ($\log \theta$ vs. $\log C$). The data gave straight lines with intercept of $\log k$. The calculated values for the equilibrium constant of adsorption was found to be 39.8×10^{-2} , 63.09×10^{-2} and 89.1×10^{-2} for methyl red, methyl orange and methyl violet, respectively.

The equilibrium constant value k is related to the standard free energy of adsorption ΔG°_{ads} by the following equation [Kliskic et al., (1997)]:

$$K = 1/55.5 \exp [-\Delta G^{\circ}_{ads}/RT] \quad (5)$$

where 55.5 is the concentration of water in solution in mol/l, R is the universal gas constant, T is the absolute temperature. The value of ΔG°_{ads} for methyl red, methyl orange, and methyl violet amount to -3.3 , -3.8 and -4.13 kJmol^{-1} , respectively. The negative values of ΔG°_{ads} indicate the spontaneous adsorption of the inhibitor on the metal surface and is usually characteristic of strong interaction with the metal surface.

Table (1): Electrochemical corrosion parameters for nickel electrode in free K_2CO_3 and inhibited K_2CO_3 solution at 25°C .

Concentration	$-E_{corr}$	$I_{corr} \times 10^4$	β_c	β_a	θ	%IE
M	mV(SCE)	m A.cm $^{-2}$	m V.dec $^{-1}$	m V.dec $^{-1}$		

0.1M K_2CO_3 +methyl red

0	445	2533	235.57	70.23		
1×10^{-5}	434	2162	219.86	69.10	0.150	14.6
5×10^{-5}	430	2059	209.95	67.89	0.190	18.7
1×10^{-4}	428	2027	208.20	66.54	0.200	20.0
5×10^{-4}	423	2017	186.15	64.40	0.200	20.3
1×10^{-3}	422	1325	181.24	58.54	0.477	47.7
5×10^{-3}	421	1243	176.08	54.56	0.509	50.9

0.1M K_2CO_3 +methyl orange

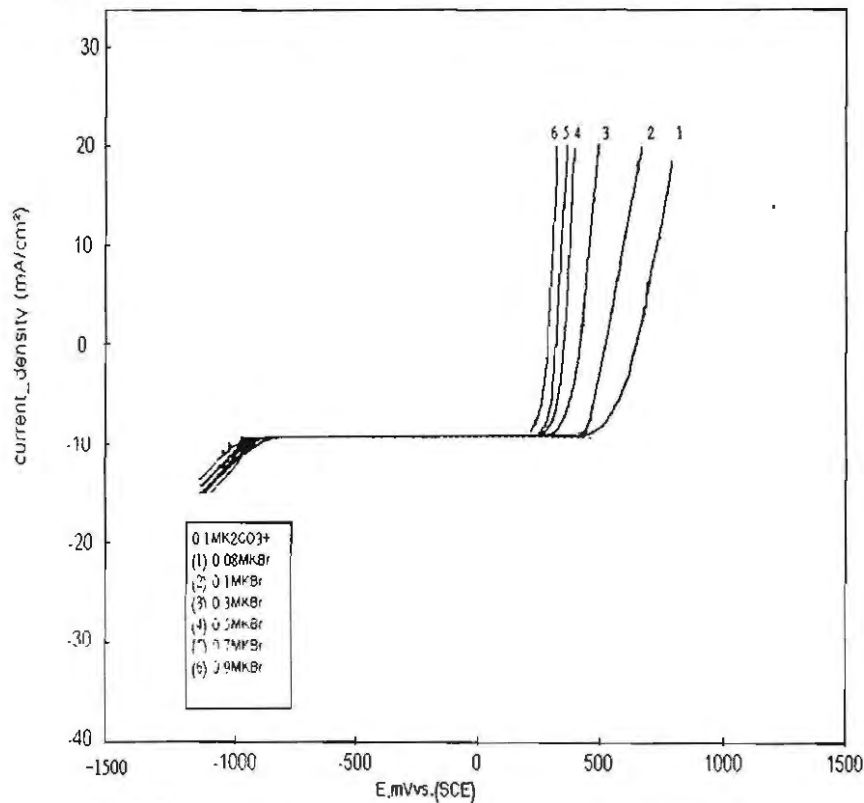
0	445	2533	235.58	70.23		
1×10^{-5}	440	2316	222.95	69.82	0.086	8.5
5×10^{-5}	437	2292	220.01	68.42	0.095	9.5
1×10^{-4}	432	2120	196.46	66.66	0.163	16.3
5×10^{-4}	430	1917	185.30	61.24	0.243	24.3
1×10^{-3}	428	1910	164.74	59.26	0.246	24.6
5×10^{-3}	426	1393	143.90	58.26	0.45	45.0

0.1M K_2CO_3 +methyl violet

0	445	2533	235.58	70.23		
1×10^{-5}	439	2475	227.77	66.57	0.023	2.3
5×10^{-5}	435	2377	219.82	62.66	0.062	6.16
1×10^{-4}	431	2158	206.43	60.82	0.148	14.8
5×10^{-4}	427	2103	192.51	59.36	0.169	16.9
1×10^{-3}	424	2075	183.88	58.97	0.181	18.1
5×10^{-3}	423	1884	175.63	55.19	0.256	25.0

3.3- Pitting corrosion studies:

The effect of some aggressive ions e.g. (Cl^- , Br^- , I^- , and $\text{S}_2\text{O}_3^{2-}$) in the pitting corrosion of nickel in 0.1M K_2CO_3 solution was examined by potentiodynamic anodic polarization measurements. Fig (3) shows the potentiodynamic anodic polarization curves of nickel electrode in 0.1M K_2CO_3 using different concentrations of KBr at scan rate $1\text{mV}\text{S}^{-1}$. Similar curves were obtained for other aggressive ions Cl^- , I^- and $\text{S}_2\text{O}_3^{2-}$ (not shown).

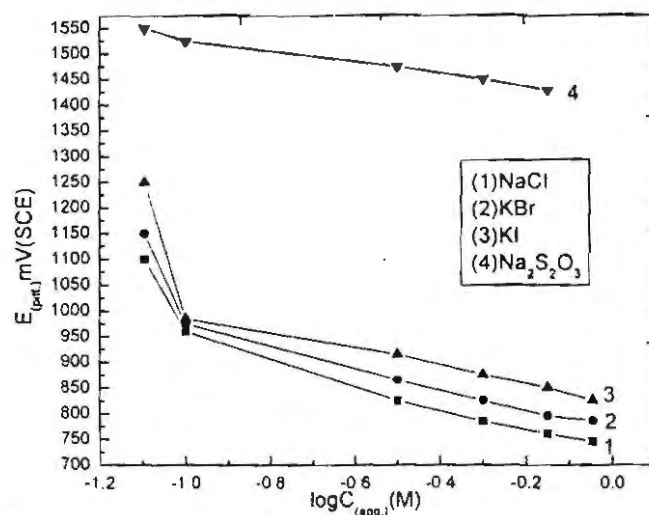


Figure(3) Potentiodynamic anodic polarization curves of Nickel in 0.1M K_2CO_3 in presence of different concentration of KBr (aggressive)

An inspection of curves in Fig (3), reveals that an addition of Br^- ions not change the shape of polarization curves recorded in halide free solution. In the concentration range of these aggressive ions studied, the metal does not exhibit an active-passive transition. However, on increasing the concentration of these ions, there is a sudden and marked increase of current density at a definite potential indicating the passivity breakdown and initiation of pitting corrosion [Kolotyarkin (1963)]. The

potential at which the sudden rise takes place is defined as the pitting potential (E_{pitt}). The higher concentration of Cl^- ion, the higher is the shift of pitting potential toward the active direction. The breakdown of passivity could be attributed to the adsorption of chloride ions on the passive film/solution interface [Abdallah (2004) and Abdallah, (1993)]. Thus, when the electrostatic field reaches a certain value, the adsorbed anions begin to penetrate into the passive film and the pitting corrosion is initiated.

Fig (4) : represents the relationship between pitting potential, E_{pitt} and logarithm of the molar concentration of the aggressive ions.



Figure(4) Relation between pitting potential and logarithm concentration of aggressive for Nickel in 0.1M K_2CO_3

From this Figure it is clear that, the tendency of nickel electrode to pitting corrosion decreases in the following order: $Cl^- > Br^- > I^- > S_2O_3^{2-}$. The shape of curves obtained indicates that:

- i) At low concentration of aggressive ions the pitting potential shifts slightly in negative direction because the aggressive ions are not sufficient to destroy completely the passivating film on the metal surface
- ii) At relatively higher concentrations of aggressive ions, E_{pitt} varies with concentration of aggressive ions according to a straight line

relationship in the form [Foroulis & Thubriker (1975) and Abd El-Haleem et al., (1976)].

$$E_{\text{pitt}} = a_1 - b_1 \log C_{\text{agg}} \quad (6)$$

where a_1 and b_1 are constants which depend on both the nature and the type of aggressive anion and of the electrode. This behavior is attributed to the destruction of the passive film formed on the metal surface and the pits formed continuously propagate and can not undergo repassivation [Abd El-Haleem, (1979)].

3.4. Inhibition of pitting corrosion:

The effect of increasing addition of the studied inhibitors on the potentiodynamic anodic polarization curves in 0.1M K_2CO_3 +0.7M KBr was studied. Similar curves were obtained but the difference; the pitting potential is shifted towards more positive direction by increasing the inhibitor concentration. This indicate that an increased resistance to pitting attack.

Fig (5) represents the relationship between E_{pitt} and $\log C_{\text{inh}}$. From the curves of this figure, the following conclusions could be drawn:
(i) An increase of inhibitor concentration results in a positive shift of E_{pitt} in accordance with the following equation:

$$E_{\text{pitt}} = a_2 + b_2 \log C_{\text{inh}} \quad (7)$$

where a_2 and b_2 are constants which depend on both the type of additive and the nature of the electrode.

ii) Inhibition afforded by these compounds decreases in the following order:

methyl red > methyl orange > methyl violet

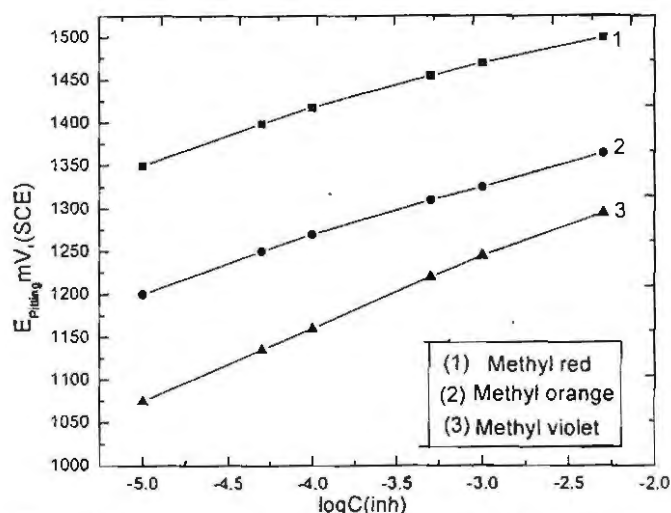


Figure (5) Relation between pitting potential and logarithm of the molar concentration of organic additive in 0.1M K_2CO_3 + 0.7M KBr

3.5. The inhibition mechanism:

The corrosion inhibition of these organic compounds towards the corrosion of nickel in 0.1M K_2CO_3 solution may be attributed to the adsorption of these compounds at the metal/solution interface where the adsorbed molecules mechanically screen the coated part of the metal surface from the action of the corrodent. The extent of the adsorption of an inhibitor depends on the nature of the metal, the mode of adsorption of the inhibitors, and the surface conditions.

The results indicated that the (%IE) of the organic compounds is more or less dependent on the nature of constituents. The orders of (%IE) and the positive shift of pitting corrosion potential decreased in the following order: methyl red > methyl orange > methyl violet. This sequence may be attributed to: methyl red and methyl orange have an active center for adsorption azo group (N=N). This lead to that methyl red and methyl orange have higher (%IE) than methyl violet, But the methyl red has higher (%IE) than methyl orange. This may be attributed to the higher basicity of methyl red. The sulphonic group (SO_3^{2-}) in methyl orange is more electron withdrawing group than carboxylic group (COO^-) present in methyl red.

4-CONCLUSION

- i) Methyl red, methyl orange, and methyl violet act as inhibitors for corrosion of nickel in 0.1M K_2CO_3 solution at 25°C.
- ii) The inhibition efficiency increases with the increase in the concentration of these inhibitors.
- iii) The inhibition is due to the adsorption of the inhibitor molecule on nickel surface.
- iv) The adsorption of these compounds on the nickel surface follows Freundlich adsorption isotherm.
- v) Methyl red, methyl orange, and methyl violet provide protection against pitting corrosion of nickel in presence of bromide ions.

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الملخص العربي

التآكل هو المشكلة الرئيسية التي تهدد فترة عمر صلاحية المعدن للإستخدام وفهم ميكانيكية التآكل يمكننا من إيجاد حل لمشاكل التآكل الحالية ومنع المشاكل المستقبلية وهذا البحث يناقش تآكل النيكل في محلول او. مولر من كربونات البوتاسيوم . تم مناقشة التركيب الكيميائي لبعض الادلة العضوية وتأثيرها على كفاءة التثبيط ولوحظ أن كفاءة تثبيط المركب يعتمد على المجموعات القطبية المستبدلة وتمت الدراسة بإستخدام الطرق التالية :

(طريقة الاستقطاب الجلفانوستاتيكي والاستقطاب البوتنشيو ديناميكي) .

وخلاصة القول أن قياسات الاستقطاب الجلفانوستاتيكي والاستقطاب البوتنشيو ديناميكي تؤيد افتراض أن تثبيط التآكل يتم عن طريق ادمصاص المثبطات على سطح النيكل . والاتفاق بين وسائل القياسات المختلفة في ترتيب كفاءة المثبطات المستخدمة يدل على صحة النتائج التي تم الحصول عليها .

