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Corrosion behavior of nickel and its alloys in HCl and its inhibition by natural rosemary oil

The corrosion behavior of nickel, Inconel 600 and Inconel 690 was studied in different concentrations of HCl solution and its inhibition by natural rosemary oil using galvanostatic polarization techniques. It was found that, HCl accelerate the corrosion of nickel and its alloys. The corrosion rate decreases in the following order Inconel 690 > Inconel 600 > Ni. This was attributed to the presence of high Cr content in the chemical composition of Inconel 690. Natural Rosemery oil inhibit the corrosion of nickel and its two alloys in 0.1 M HCl. The inhibition efficiency increases with increasing the concentration of this oil which act as an inhibitor of the mixed type. The inhibitive effect of this oil was explain in view of adsorption on the metal surface. The adsorption process follows Langmuir adsorption isotherm. The addition of this oil to the potentiodynamic anodic polarization curves of nickel and its two alloys in chloride solutions shift the pitting potential to more noble direction, indicating an increased resistance to pitting attack.

Key words: *Rosemary oil, nickel, Inconel 600, Inconel 690, corrosion inhibitors, pitting corrosion*

1. INTRODUCTION:

Acid solutions are commonly used in chemical industry to remove mill scales from metallic surface. The addition of inhibitors effectively secures the metal against an acid attack. Most acid inhibitors are organic compounds containing nitrogen, oxygen and/or sulphur. These compounds are adsorbed on the metallic surface blocking the active corrosion sites[1-4]. Due to the toxicity of organic compound, there has been increasing search for agree corrosion inhibitors [5,6]. Inhibitors in this class are those that are environmentally friendly and gotten from nature (product) such as plant extract [7-12].

Previous works [13] reported successful use of the natural clove oil as corrosion inhibitor for nickel and its alloys in HCl solution. Extract of Hcnna (Lawsonia) as corrosion inhibitors of C-steel, nickel, and zinc in acidic, neutral and alkaline solution.

This work is devoted to examining the natural rosemary oil as an inhibitor for corrosion of nickel and its alloys in 0.1M HCl solution. Galvanostatic and potentiodynamic anodic polarization were used in this study.

2. EXPERIMENTAL METHODS

The chemical composition of nickel and two alloys namely, Inconel 600 and Inconel 690 are presented in Table 1. These electrodes were fixed to Pyrex glass tubing using neutral wax. Exposed surface areas were 0.126 cm^2 for nickel, 1.43cm^2 for inconel 600 and, 0.18 cm^2 for inconel 690. Electrical contacts were made through thick copper wires soldered to the end of electrodes not exposed to the solution. The electrodes were successively abraded with the finest grade emery paper, degreased with acetone and finally washed with twice-distilled water, complete wetting of the surface was taken as indication of its cleanliness. All chemicals used were of A.R. quality. The solutions were prepared using twice-distilled water and no trials were made to deareate them. The electrolytic cell was all Pyrex and described elsewhere [15]. The experiments were carried out at 25 ± 1^{o}C.

Table 1: Chemical composition of the test alloys

Samples	Ni	Fe	Cr	Cu	Si	Al	Ti	Mn	C	Others
Nickel	99.9	-	-	-	-	-	-	-	-	0.1
Inconel 600	73.42	9.33	16.1	1.03	0.118	0.28	0.24	0.38	0.04	**P** 0.007 **S** 0.006
Inconel 690	59.79	9.14	30.06	-	-	0.36	0.26	-	0.033	-

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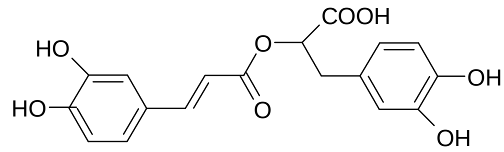
Potentiostatic and potentiodynamic anodic polarization experiments were carried out using PS remote potentiostat with PS6 software for calculation of some corrosion parameters e.g., corrosion current density (I_{corr}), corrosion potential (E_{corr}) and Tafel constant (ba & bc). The corrosion parameters were calculated from the intercept of the anodic and cathodic Tafel lines. A three compartment cell with a saturated calomel reference electrode (SCE) and a platinum foil auxiliary electrode was used. The inhibition efficiency IE was calculated using the equation:

$$IE = \left[\frac{I_{free} - I_{add}}{I_{free}} \right] \times 100 \qquad (1)$$

where I_{free} and I_{add} are the corrosion current densities in free and inhibited acid, respectively.

Rosemary oil:

The plant contains some tannic acid and the main chemical composition of rosemary oil is rosmarinic acid (is a phenolic compound[16].



3- RESULTS AND DISCUSSION

3.1 Galvanostatic polarization

3.1.1. Effect of acid concentration

Figure 1 shows the anodic and cathodic polarization curves for nickel electrode in different concentrations of HCl solutions. Similar curves were obtained for the other two samples Inconel 600 and Inconel 690 (not shown). Inspection of the curves in Fig. (1) shows that at first transition region in which the potential increases (anodic polarization) or decreases (cathodic polarization) slowly with current density, followed by a rapid linear build up of the potential with current density (the Tafel region). The transition region starts from the corrosion potential and extends to the beginning of the Tafel region and characterized by simultaneous occurrence of cathodic hydrogen evolution and anodic dissolution of the electrode samples [17].

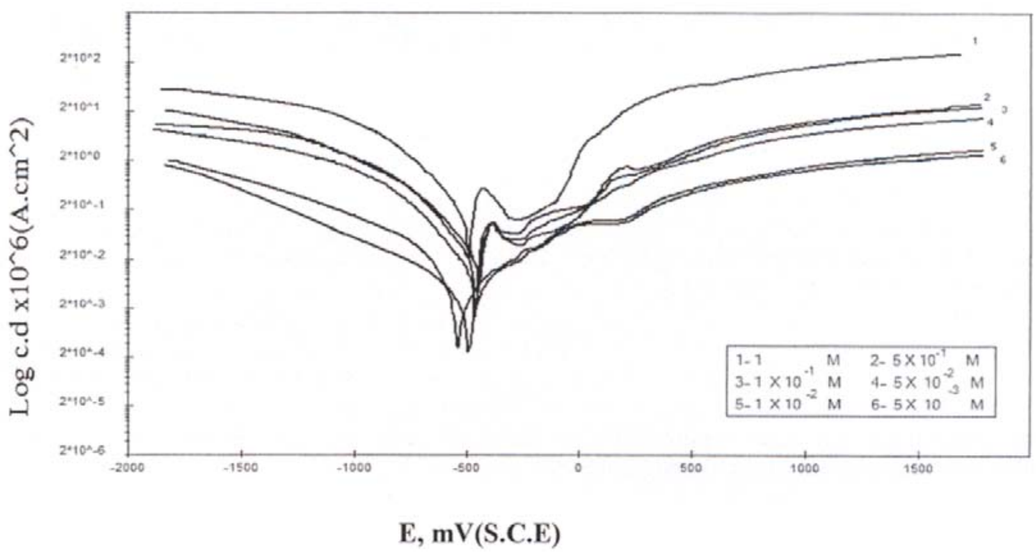


Fig. 1): Anodic and cathodic polarization curves of Ni metal in different concentrations of HCl solution

The effect of acid concentration on the corrosion parameters such as corrosion potential ($E_{corr.}$), corrosion current density ($I_{corr.}$) corrosion rate (R_{corr}) and anodic (ba), cathodic (bc) Tafel slopes are listed in Table 2. It is clear that from Table 2. As the concentration of HCl increases, the values of corrosion potential (E_{corr}) is almost nearly constant, I_{corr} increases and consequently R_{corr} increases. This means that hydrochloric acid accelerates the dissolution of Ni and its alloys. Also, it is clear that at one and the same concentration of HCl solution the corrosion rate decreases in the following order:

Inconel 690 > Inconel 600 > Ni

This indicates that Inconel 690 is more resistance to corrosion in HCl than Inconel 600 and Ni. This behaviour will be discussed later.

Table (2): Electrochemical parameters obtained from anodic and cathodic polarization curves of Ni metal, Inconel 600 and Inconel 690 in different concentrations of HCl at 25ºC.

Elctrode Sample	Acid Conc. *M*	E_{CORR} mV (S.C.E)	I_{corr} ($mA.Cm^{-2}$)	R_{corr} (mm/year)	ba ($mV. dec^{-1}$)	- bc ($mV. dec^{-1}$)
Ni metal	1	-490	0.4050	8.835	318	227
	0.5	-460	0.3580	6.890	340	390
	0.1	-446	0.2562	5.584	442	440
	0.05	-460	0.1950	4.248	513	469
	0.01	-545	0.0686	1.494	717	578
	0.005	-490	0.0300	0.570	796	606
Inconel 600	1	-495	0.3791	8.2629	438	209
	0.5	-468	0.3100	5.4231	544	290
	0.1	-450	0.2013	4.3895	643	386
	0.05	-468	0.1500	3.2175	721	456
	0.01	-420	0.0445	0.9702	791	543
	0.005	-485	0.0160	0.3494	850	655
Inconel 690	1	-490	0.2592	5.4339	550	128
	0.5	-460	0.1983	4.3234	615	212
	0.1	-460	0.1754	3.8289	680	256
	0.05	-460	0.0980	2.1720	730	276
	0.01	-545	0.0272	0.5923	858	373
	0.005	-490	0.0063	0.1368	896	397

3.1.2. Effect of Rosemary oil concentration:

The effect of increasing concentration of rosemary oil on the anodic and cathodic polarization carries of Ni in 0.1 M HCl is represented in Fig.2. Similar curves were obtained in case of Inconel 600 and Inconel 650 (not shown).

Inspection of this figure reveals that the polarization curves are shifted toward more negative potential and less current density upon addition of Rosemary oil. This result confirms the inhibitive action of the Rosemary oil toward the acid corrosion of nickel and its alloys used.

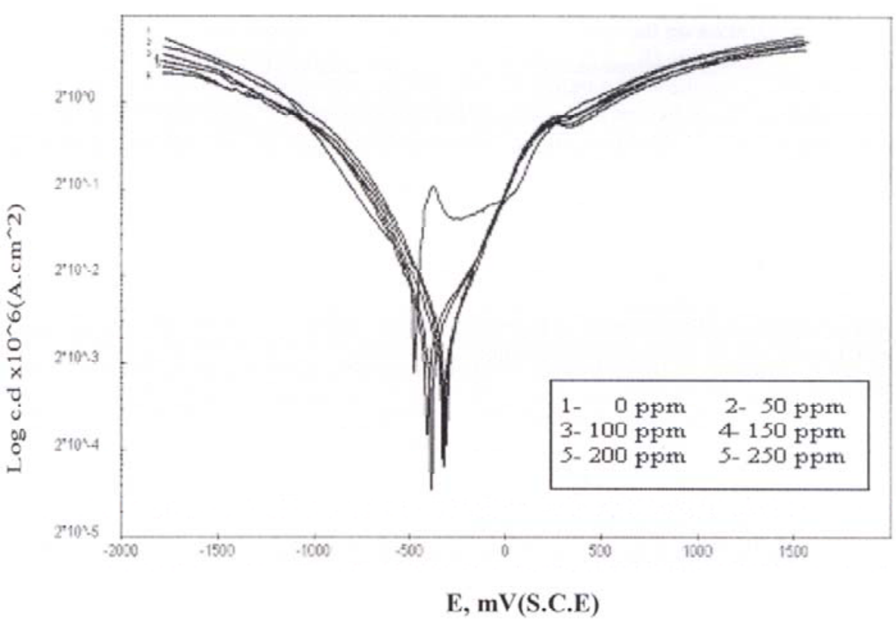


Fig. 2: Anodic and cathodic polarization curves of Ni in 0.1M HCl containing different concentrations of Rosemary Oil.

The corrosion parameters of nickel, Inconel 600 and Inconel 690 in 0.1*M* HCl containing different concentrations of Rosemary oil were calculated and presented in Table 3.

Inspection of Table 3 reveals that. As the concentration of Rosemary oil increases, E_{corr} is shifted toward more positive direction, I_{corr} decreases and hence I.E. increases. This indicates that the inhibitive effect of this oil and the I.E. increases with increasing Rosemary oil concentration. Further inspection of Table 3 reveals that the values of anodic (ba) and cathodic (bc) decreases with increasing the concentration of Rosemary oil. This means that these compounds influence both cathodic and anodic process [18]. However, the data suggested that these compounds act mainly as mixed type inhibitor.

Table (3): Electrochemical parameters obtained from anodic and cathodic polarization curves of Ni metal, Inconel 600 and Inconel 690 in 0.1 M of HCl and different concentrations of Rosemary Oil at 25ºC.

Electrode / Sample	Inhibitor ppm	E_{corr} mV (S.C.E)	I_{corr} ($mA.Cm^{-2}$)	R_{corr} (mm/y)	ba ($mV.dec^{-1}$)	- bc ($mV. dec^{-1}$)	I.E %	θ
Ni	0	-446	0.2562	5.5840	442	440	-	-
	50	-335	0.0588	1.2821	199	260	77.04	0.7704
	100	-317	0.0232	0.8741	182	236	87.41	0.8741
	150	-395	0.0256	0.5595	216	195	89.98	0.8998
	200	-334	0.0189	0.4128	187	222	92.61	0.9261
	250	-412	0.0172	0.3752	202	165	93.28	0.9328
Inconel 600	0	-450	0.2013	4.3895	643	386	-	-
	50	-360	0.0331	0.7218	200	278	83.56	0.8356
	100	-251	0.0180	0.3915	188	227	91.06	0.9106
	150	-199	0.0140	0.3050	200	236	93.04	0.9304
	200	-273	0.0125	0.2728	196	236	93.79	0.9379
	250	-312	0.0090	0.1962	189	258	95.53	0.9553
Inconel 690	0	-460	0.17540	3.8289	680	256	-	-
	50	-360	0.00772	0.1685	262	277	95.60	0.9560
	100	-382	0.00377	0.0823	287	237	97.85	0.9785
	150	-412	0.00367	0.0800	265	219	97.91	0.9791
	200	-420	0.00260	0.0567	322	179	98.52	0.9852
	250	-440	0.00033	0.0073	344	189	99.81	0.9981

3.1.3. Adsorption isotherm:

The values of surface coverage (θ) were evaluated at different concentrations of the Rosemary oil in 0.1M HCl solution using the following equation:

$$\theta = 1 - \frac{I_{add}}{I_{free}} \qquad (2)$$

where I_{add} and I_{free} are defined previously. The values of θ have been inserted into Table 3. The degree of surface coverage θ was found to increase with increasing the concentration of Rosemary oil. This indicates that the inhibitive action of Rosemary oil toward the acid corrosion of nickel and its alloys could be attributed to the adsorption of its compound onto the surface of the metal. The adsorbed layer acts as a barrier between the metal surface and aggressive solution leading to a decrease in the corrosion rate.

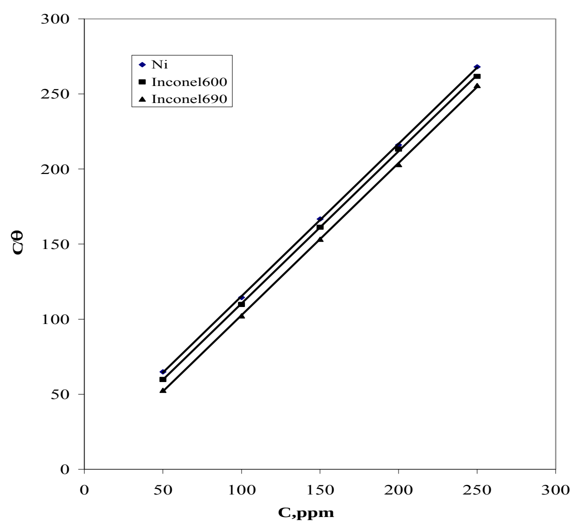


Fig. 3: Langmuir adsorption isotherm for Ni, Inconel 600 and Inconel 690 in present of Rosmary Oil

Table (4): Equilibrium constant and adsorption free energy of Rosemary Oil adsorbed on Ni metal, Inconel 600 and Inconel 690

Electrode	K	$-\Delta G_{ads}$ kJ .mol^{-1}
Ni	7.3×10^{-2}	13.472
Inconel 600	11.08×10^{-2}	14.501
Inconel 690	78.12×10^{-2}	19.339

Attempts were made to fit the θ values to various isotherms including Langmuir, Temkin, Framkin, Freundlich and Flory Huggins. By far the best fit is obtained with the Langmuir isotherm. Langmuir adsorption isotherm was found to be the best description of the adsorption behavior of the studied rosemary oil among several adsorption isotherms were assessed. Langmuir adsorption isotherm described by the following equation:

$$\frac{C_{inh}}{\theta} = \frac{1}{k} + C_{inh} \quad (3)$$

$$K = \frac{1}{55.5}\exp\left(-\frac{\Delta G_{ads}}{RT}\right) \quad (4)$$

where C_{inh} is the inhibitor concentration, K is the adsorption coefficient and ΔG_{ads} is the standard adsorption. Fig. 3. represents the relation between C/θ and C. Straight line relationship were obtained indicating that the adsorption of rosemary oil on the nickel and its two alloys follows Langmuir adsorption isotherm and consequently, there is no interaction between the molecules adsorbed at the metal surface.

The values of K and ΔG_{ads} of the inhibitors adsorbed on the surface Ni, Inconel 600 and Inconel 690 were calculated and listed in table (4).

The standard free energy of adsorption is associated with water adsorption/desorption equilibrium which forms an important part in the overall free change of adsorption.

The negative value of ΔG_{ads} indicates that the rosemary oil is spontaneously adsorbed on the metal surface.

3.2. Potentiodynamic anodic polarization:

3.2.1 Effect of chloride ion concentrations

The effect of the NaCl concentration in the pitting corrosion of nickel and its alloys in 0.1M HCl solution was examined by potentiodynamic anodic polarization technique.

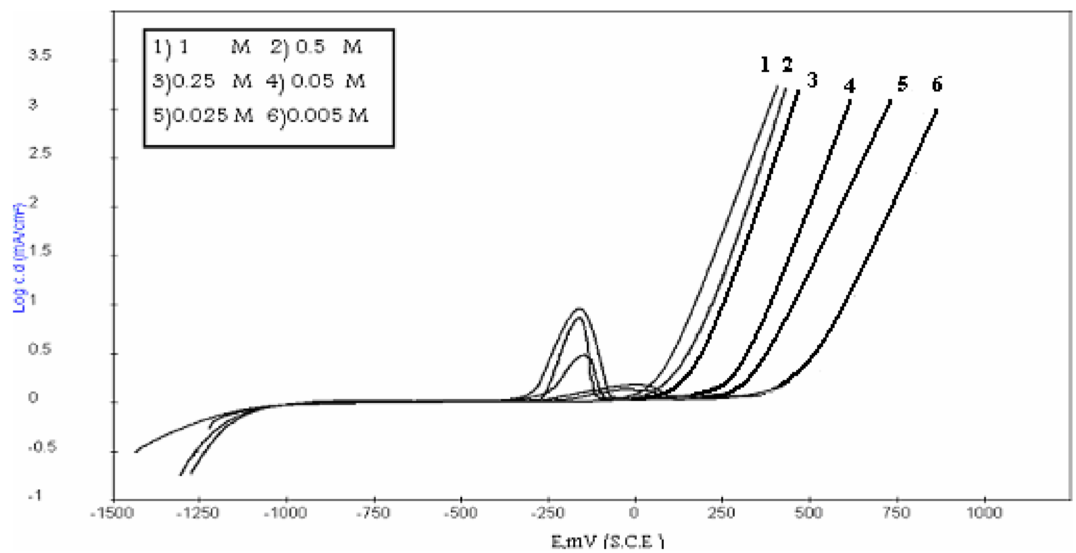


Fig. (4): Potentiodynamic anodic polarization curves of Ni metal in different concentrations of NaCl solutions

Fig.4. shows the potentiodynamic anodic polarization curves of nickel electrode in 0.1M at a scan rate 1mV s^{-1}. The slow scan rate permits that the pitting inhibition occurs at less positive potential [19]. It is clear from the results that in the concentration range of NaCl studied, there is only one anodic peak. This peak may be correspond to oxidation of Ni to $Ni(OH)_2$ according to the following reaction:

$$Ni + 2H_2O \rightarrow Ni(OH)_2 + 2H^+ + 2e \quad (5)$$

However, on increasing the concentration of Cl^- ion, there is a sudden and marked increase of current density at definite potential indicating the passivity breakdown and initiation of pitting corrosion [20]. 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 towards the active direction.

The breakdown of passivity could be attributed to the adsorption of chloride ions on the passive film formed on the steel surface, which create an electrostatic field across film/solution interface [21, 22]. 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.

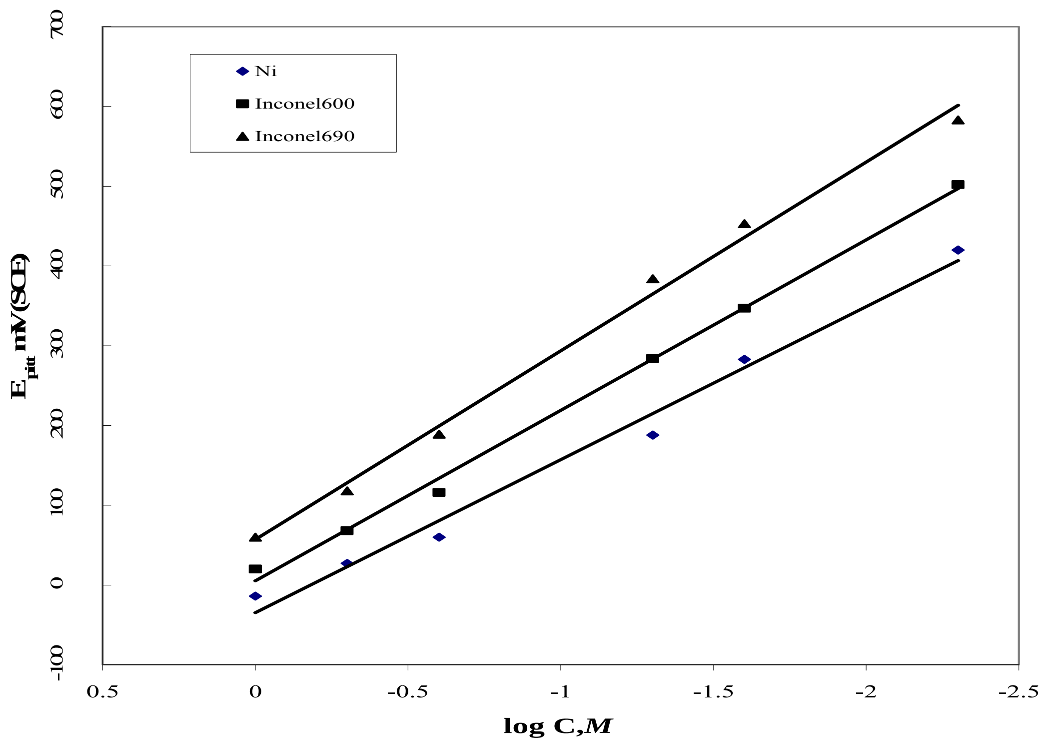


Fig. 5: The relationship between pitting potential and logarithm the concentration of NaCl solution for Ni metal and Inconel 600 and Inconel 690

The dependence of the pitting potential E_{pitt}, on the Cl^- ion concentrations is illustrated in Fig. 4. Straight line relationship is obtained obeys the equation:

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

where a_1 and b_1 are constants which depends on the nature of the metal and the type of the aggressive ions. Also at one and the same Cl^- ion concentration the shifts of E_{pitt} to loss noble values decrease in the order:

Inconel 690 > Inconel 600 > Ni

This order reflects that, Inconel 690 is more resistance to pitting attack than Inconel 600 and Ni. This behavior is similar to that obtained in potentiodynamic polarization of nickel and its alloys in HCl solution.

This behavior could be attributed to the higher Cr content of Inconel 690. The presence of chromium plays an important role for increased resistance to pitting and general attack due to formation of thick film of Cr_2O_3

3.2.2. Inhibition of pitting corrosion:

The effect of increasing concentration of Rosemary oil on the potentiodynamic anodic polarization of nickel electrode in 0.25M NaCl solution at scan rate $1 mVs^{-1}$ is illustrated in Fig. 6. Similar curves were obtained for other two alloys, Inconel 600 and Inconel 690 (not shown). It was found that, increasing the concentration of Rosemary oil causes a shift of the pitting potential into noble (positive) direction. This indicates the inhibitive of effect of this oil toward pitting corrosion.

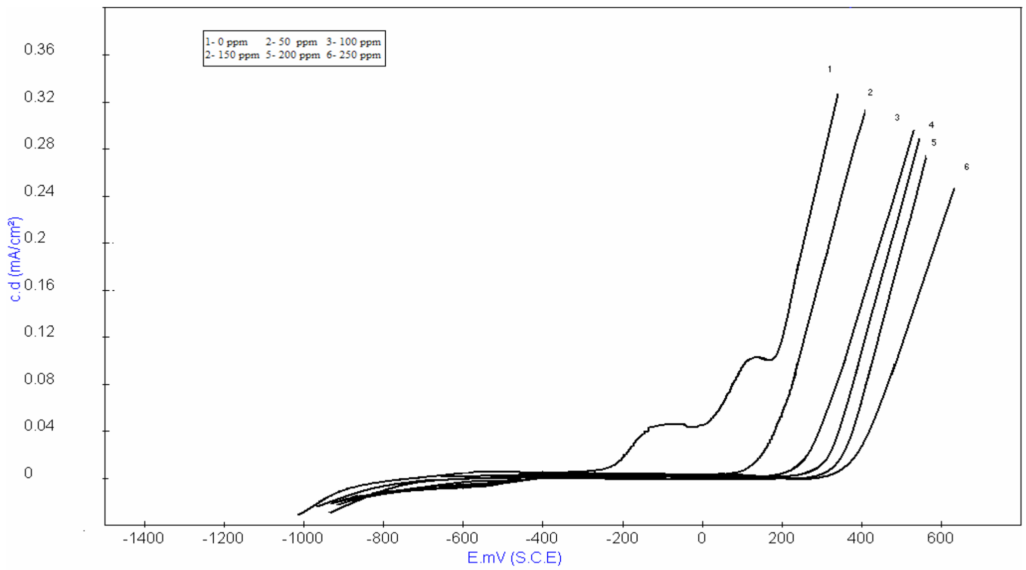


Fig. 6: Potentiodynamic anodic polarization curves of Ni 0.25 M NaCl solution containing different concentrations of Rosemary Oil

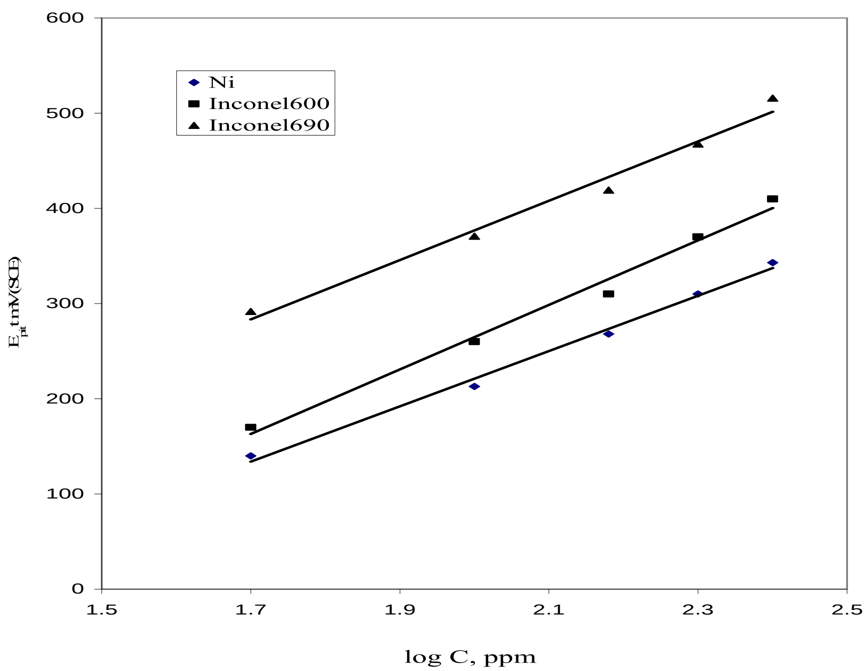


Fig. 7: The relationship between pitting potential and logarithm the concentration of Rosemary oil in 0.25 M of NaCl solution for Ni Inconel 600 and Inconel 690

Fig. 7 represents the relationship between E_{pitt} and logarithm of concentrations of Rosemary oil. It is clear from this Fig that, as the concentration of additives increases the pitting potential shifted to more positive values in accordance with the following equation:

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

where a_2 and b_2 are constants depending on the type of additives used and the nature of the electrode. The positive shift of E_{pitt} indicates the increased resistance to pitting attack. From the above results, it is found that the Rosemary oil acts as pitting corrosion inhibitors for nickel, Inconel 600 and Inconel 690.

Mechanism of inhibition

The inhibitive action of naturally rosemary oil toward the general and pitting corrosion of nickel Inconel 600 and Inconel 690 could be attributed to the adsorption of its component on the metal surface. The adsorbed layer act as a barrier between the metal surface and aggressive solution leading to a decrease in the corrosion rate.

The main constituent of the chemical structure of rosemaric oil is rosemaric acid which contains polyphenolic compounds readily form complex with di- and trivalent metal ions (23). The inhibitor action of this compound could be explained due to the formation of complexes in the form of chelate with nickel ions in the solution. The Ni^{2+} ion is coordinated with the phenolic groups in the terminal side in each molecule taking phase as shown Fig. 8

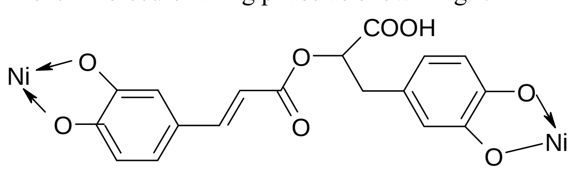


Fig. (8): Chemical structure of the complex formed.

The presence of more than one active centre in the chemical composition of oils forces the rosemary oil to be horizontally orented at the metal surface, which increases the surface coverage and consequently increase the inhibition efficiency.

CONCLUSIONS

1. HCl accelerates the corrosion of nickel, Inconel 600 and Inconel 690.
2. Inconel 690 is more resistant to corrosion in HCl than inconel 600 and Ni due to the presence of high Cr content.
3. Rosemary oil acts as a good corrosion inhibitor for nickel and its alloys in 0.1M HCl solution.
4. The inhibition action of the rosemary oil was attributed to the adsorption of its oil on the nickel surface.
5. The adsorption of this oil on the metal surface follows Langmuir adsorption isotherm.
6. Rosemary oil inhibit the pitting corrosion of nickel and its alloys in chloride containing solution.

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