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# Electrochemical studies on the corrosion behavior of nickel in some aqueous media.

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It is known that nickel and nickel alloys are important materials for the design vessels in different industrial processes. Nickel electrode is also used in different energy producing cells in which aqueous or non-aqueous solutions are used as electrolytes. In such aspect, the corrosion and corrosion inhibition of nickel in different media become very interesting and important owing to its wide applicability in industry and domestic life. The purpose of the present investigation is to study the corrosion and corrosion inhibition of nickel in sulphuric acid and sodium hydroxide solutions in absence and presence of some pyridinone derivatives as corrosion inhibitors for dissolution of nickel in  $H_2SO_4$  and some natural oils as corrosion inhibitors for dissolution of nickel in  $NaOH$  was examined. The thesis comprises five main chapters: -Chapter (I) is concerned with an introduction reviewing concisely the relevant literature related to the project of investigation. Chapter (II) deals with experimental part, which includes, types of electrodes that are used in different techniques, methods of preparation of materials of various solutions used. Also experimental techniques contain the instruments and the procedure used for corrosion measurements, using the chemical technique (open circuit potential method) and the electrochemical techniques (galvanostatic polarization method and Tafel extrapolation method). Chapter (III) is divided into three sections: section (A) is concerned with potential-time curves for the nickel electrode in different concentrations of sulphuric acid. Passivity and oxide film formation is found to decrease with acid concentration. Passive film is more predominate in the dilute acid solutions. The steady state potential is shifted to more negative values with increasing  $H_2SO_4$  concentrations. The effects of additions of corrosive salts ( $NaCl$  and  $NaBr$ ) destroy the passive film formed on Ni in dilute sulphuric acid solutions. The presences of these salts lead to breakdown of the formed passive film on the metal surface and initiate pitting corrosion. Also, the presence of pyridinone derivatives acts as inhibitors and reduces the dissolution of nickel in  $H_2SO_4$ . It is found that the steady state potential is shifted to more positive values with increasing the concentration of the organic additives indicating a toleration of corrosion process. The order of the inhibition effect is decreased in the following order: Compound IV > compound III > compound II > compound I. Section (B): includes Galvanostatic polarization of the Ni in  $H_2SO_4$  solutions. The following conclusion can be drawn: -1- The galvanostatic polarization technique under a constant polarizing current was used to study the

electrochemical anodic behavior of nickel electrode in different concentration of H<sub>2</sub>SO<sub>4</sub> solutions. The general shape of the polarization curve is found to depend on the magnitude of the polarized current density, the acid concentration and the temperature of the solution. The data of the polarization curves are characterized by:

- (i) A rapid and almost linear change in potential with time, due to the decay of hydrogen overpotential and subsequent charging of the electrical double layer at the metal/solution interface.
- (ii) A relatively large distinct potential arrest, a, corresponding to anodic dissolution of the nickel to Ni<sup>+</sup> ions
- (iii) Second potential arrest, b, corresponding to the electro-oxidation of Ni<sup>+</sup> ions to Ni<sup>2+</sup> ions.
- (iv) A linear rise in the potential indicating the onset of passivity due to the formation of Ni<sub>2</sub>O<sub>3</sub>,
- (v) Finally, a deviation from linearity to reach steady-state potential value attributed to oxygen evolution reaction.

2-The duration time of each arrest decreases with increasing the current density and the electrolyte concentration. Also, the electrode potentials corresponding to the different arrests were found to depend on the magnitude of the polarizing current density, the acid concentration and the solution temperature. The duration time,  $\tau$ , of the dissolution process was found to increase with the decrease of the solution acidity and the current density and also with the increase of solution temperature.

3- In the presence of additions of small concentration of Cl<sup>-</sup> and Br<sup>-</sup> ions, the passivity of nickel electrode tolerates the action of these aggressive ions up to certain concentration which depends on the electrolyte bulk concentration.

4- The increase in Cl<sup>-</sup> or Br<sup>-</sup> ions concentration induce oscillations at a definite potentials which is defined as the pitting potential at which initiation of pitting corrosion is occurred.

5- The presence of pyridinone derivatives act as inhibitors for pitting corrosion for nickel in  $1 \times 10^{-2}$  M H<sub>2</sub>SO<sub>4</sub> containing  $5 \times 10^{-3}$  M NaCl and shifts the pitting potential towards more positive values.

6-The pitting potential shifts towards more positive values with increasing inhibitor concentration according to the relation:  $E_{pit} = a + b \log C_{inh}$  where a and b are constants.

7- The concentration of the inhibitors causes the marked shift in the pitting corrosion potential in to the noble direction increases in the order: compound IV > compound III > compound II > compound I

Section(C): In which Tafel polarization technique is used to study the kinetics of dissolution of nickel in H<sub>2</sub>SO<sub>4</sub>. The results indicate that:

- 1-The anodic dissolution process is considered as a first order reaction for Ni dissolution, while the cathodic reaction is kinetically second order for hydrogen evolution.
- 2-As the acid concentration increases both anodic and cathodic currents increase.
- 3-The increase in the  $i_{corr}$  with H<sub>2</sub>SO<sub>4</sub> concentration follows the equation:  $\log i_{corr} = a_1 + b_1 \log C_{H_2SO_4}$  where  $a_1$  and  $b_1$  are constants. The increase in the corrosion current density with acid concentration could be related to the decrease in the polarization resistance of Ni.
- 4- The corrosion potential is shifted to more negative values confirming the destruction process.
- 5-The presence of some pyridinone derivatives act as inhibitors for dissolution of nickel in H<sub>2</sub>SO<sub>4</sub>. It shifts the corrosion potentials to more positive values. Also, the corrosion current density decreases and consequently, the inhibition efficiency increases.
- 6-The inhibition can be related to the adsorption of the inhibitor molecules on the nickel surface and obeyed Langmuir adsorption isotherm.

Chapter (IV): includes three sections: Section (A) includes the oxide film formation and growth under open circuit potential measurements of the nickel electrode in different

concentrations of sodium hydroxide. It is found that

- 1-The steady state potential is shifted to less negative values with increasing concentrations of NaOH solutions due to dissolution of oxide film with raising the pH of solution.
- 2-The presence of (Cl<sup>-</sup>) destructs the passive film formed of Ni in NaOH.
- 3-The addition of some natural oil retards the destruction and repair formed passive film on nickel in NaOH.
- 3-The steady state potential is shifted to more positive values with concentration of the additives.
- 4- The order of the positive shift is decreased in the following order: sesame oil > water cress oil > wheat germ oil > almond oil

Section (B) includes the galvanostatic polarization the nickel electrode in NaOH solutions. The following conclusion can be drawn:

- 1-The linear rise in the potential with time is due to the formation of barrier oxide film, while, the deviation from linearity at steady state potential is attributed to oxygen evolution reaction.
- 2-The presence of an arrest with duration time decreases with increasing current density and the concentration of sodium hydroxide, while, the rate of oxide film formation increases with concentration.
- 3- The duration time increases with temperature while the rate of oxide film formation decreases
- 4- The presence of lower concentrations of Cl<sup>-</sup> ions has no effect on the mechanism of nickel passivation. An increase in Cl<sup>-</sup> ions causes a breakdown in the passive region (rising part in E-time curve). This could be attributed to the destruction of the passivity by Cl<sup>-</sup> ions and the initiation of pitting corrosion.
- 5- Presence of some natural oils shift the active dissolution potential to the more positive direction and the time required to passivate the Ni electrode is decreased.
- 6-The order of retardation of Ni dissolution in NaOH by natural oils has the order: sesame oil > water cress oil > wheat germ oil > almond oil

Section (C) includes Tafel extrapolation technique of nickel in different NaOH solution. The following conclusion can be drawn:

- 1- The value of  $i_{corr}$  is increased with an increase in NaOH concentration according to the following equation:  $\log i_{corr} = a_1 + b_1 \log C_{NaOH}$  (4C. 1) where  $a_1$  and  $b_1$  are constants.
- 2-The free corrosion potential,  $E_{corr}$ , is shifted to more negative direction as the alkali concentration is increased according to the relation:  $E_{corr} = E_1 - 0.059/z \log C_{NaOH}$  where  $E_1$  is the free corrosion of Ni electrode in 1 M NaOH which amounts to -283 mV(SCE).
- 2-The anodic dissolution process and the cathodic reaction are kinetically considered as first order for each reaction.
- 3-The increase in the temperature caused an increase in both the anodic and cathodic current densities, indicating that the rate of hydrogen evolution and metal dissolution, that is, the corrosion current density  $i_{corr}$ , are increased.
- 4-The variation of corrosion current density,  $i_{corr}$  versus the concentration of the inhibitors  $C_{inh}$ , according to the equation:  $\log i_{corr} = a_3 - b_3 \log C_{inh}$  where  $a_3$  and  $b_3$  are constants.
- 5-The presence of natural oils as inhibitors cause a decrease in the rates of anodic dissolution reaction and hydrogen gas evolution. This may be attributed to adsorption of these compounds over the nickel surface.
- 6-The adsorption isotherm obeyed Freundlich adsorption isotherm according to the following equation.
- 7- The inhibition efficiencies of the tested oils decreases in the following order: - Sesame oil > water cress oil > wheat germ oil > almond oil.