Summary

Stainless steels are used as construction materials for corrosion resistant equipment in most of the major industries, particularly in the nuclear, petroleum, power, food production, medical, chemical and electrochemical industries. The crown ethers constitute a potential class of corrosion inhibitors. Thus, the aim of the present work is to study:

a) The effect of some selected crown ethers on the corrosion rate of different types of stainless steels.
b) The effect of alloying elements on the corrosion resistance of the used stainless steels.

The thesis comprises three main chapters; introduction, experimental work and results & discussion. ***The introduction part*** deals with the following fields of interest:

- Electrochemical theory of corrosion
- Classification of corrosion and Corrosion monitoring techniques.
- Inhibition of stainless steel corrosion in aqueous solutions.
- Crown ethers as corrosion inhibitors.
- Aim of the present work.

Chapter two deals with the experimental work part. It includes the chemical composition of the investigated stainless steels (430, 304 & 316SS); preparation of the hydrochloric acid solutions as corrosive medium; the used crown ethers solutions (DB18C6, Kry-22DD, Kry-222 & DB24C8) and the techniques used for the corrosion measurements [loss in mass, galvanostatic polarization, scanning electron microscopy (SEM) and x-ray photoelectron spectroscopic analysis (XPS) techniques].

The results obtained and their interpretations are shown in ***chapter three*** under six separated sections; (A), (B), (C), (D), (E) and (F).

Section (A): contains the results of loss in mass technique of different types of stainless steel in 2M HCl solutions containing different concentrations of the investigated crown ethers at different temperatures. These results revealed that:

- In general, for all types of stainless steel, by increasing the concentration of the investigated crown ethers (from $1x10^{-7}M$ to $1.1x10^{-6}M$), the corrosion rate of stainless steels was decreased.
- The mass loss values of different types of stainless steel in absence and presence of crown ethers obeyed the following trend:

  430SS > 304SS > 316SS
- The effectiveness of crown ethers as corrosion inhibitors for all types of stainless steel varies according to the following order:

  DB18C6 < Kry-22DD < Kry-222 < DB24C8
- The mass loss values for all types of stainless steel in absence and presence of crown ethers increase by increasing temperature.

The results showed that the adsorption of crown ethers on the surface of stainless steels obeyed Temkin's adsorption isotherm. The results were treated to obtain the free energy of adsorption (ΔG_{ads}) and the equilibrium adsorption constant (K) using the kinetic model and Temkin's adsorption isotherm. Inspection of these data showed that the values of (ΔG°_{ads}) and its negative sign indicated that the adsorption of crown ethers on the surface of the different types of stainless steel is proceeding spontaneously and is accompanied by a highly-efficient adsorption and the values of (ΔG°_{ads}) obtained from El-Awady model are comparable with those obtained from Temkin's isotherms.

The effect of temperature on the corrosion rate was studied. It was found that the mass loss values increase with raising the temperature from 303K to 333K. The increase in weight loss values with increasing temperature is suggestive of physical adsorption of crown ethers on the surface of stainless steels. The values of corrosion rate which obtained at different temperatures permit the calculation of the Arrhenius activation energy (E_a^*). Free energies of activation (ΔG^*) were calculated by applying the transition state equation. Moreover, the enthalpy (ΔH^*) and the entropy of activation (ΔS^*) parameters were calculated. It was concluded from thermodynamic parameters of activation that:

- As the activation energy values (E_a^*) were increased by increasing the concentration of crown ethers, the dissolution of stainless steels is activation controlled.
- The increase of (ΔH^*) and (ΔG^*) values in the presence of crown ethers in 2M HCl implies that energy barrier of the corrosion reaction in the presence of

crown ethers increases. On the other hand (ΔS^*) values are lower and have negative values due to the decrease in the disordering in going from reactants to the activated complexes.

- The increase in (ΔG^*) values with increasing temperature and the constantly values of (ΔH^*) indicated that the mechanism of the corrosion reaction was not changed by raising the temperatures and the low values of (ΔH^*) suggested that the crown ethers are physically adsorbed.
- The increase of (IE%) with the increase in the immersion time may be attributed to the formation of a barrier passive film. The order of the inhibition efficiencies of crown ethers as gathered from the increase in (E_a^*) and (ΔH^*) values and decrease in (ΔS^*) values for stainless steels is:

DB18C6 < Kry-22DD < Kry-222 < DB24C8

Section (B): contains the results of galvanostatic polarization measurements of stainless steels in 2M HCl in absence and presence of crown ethers. These results permitted to conclude that:

- Galvanostatic anodic and cathodic polarization curves for all types of stainless steel exhibit Tafel behavior. Addition of crown ethers caused a shift in both cathodic and anodic polarization curves towards the lower values. The values of Tafel slopes (β_a & β_c) are comparable; this suggesting that the crown ethers behave as mixed type inhibitors, but the cathode is more polarized when the external current was applied.
- The corrosion current density ($I_{corr.}$) values decreases with increasing concentration of crown ethers, which indicated that the presence of these compounds retards the dissolution of stainless steels.
- The order of inhibition efficiency of crown ethers obeys this trend:

DB24C8 > Kry-222 > Kry-22DD > DB18C6

This is also in agreement with the observed order of corrosion inhibition which is achieved loss in mass technique. Also, the data obtained indicted that these compounds are adsorbed on the surface of stainless steel according to Temkin's adsorption isotherm. Also, this agrees with the results obtained from loss in mass technique in section (A).

Section (C): contains the results of scanning electron microscopy (SEM). The morphology of the corroded surface of each specimen was studied using scanning electron microscope (SEM). These results revealed that the surface was damaged appreciably owing to the corrosion in the presence of ($5x10^{-7}$ M) of DB18C6 as example, but is still in better conditions than the specimen exposed to the corrosive medium in the absence of inhibitors. When the concentration was increased to ($9x10^{-7}$ M), there was much less damage to the surface presumably as a result of the presence of a protective film of the inhibitor on the surface. Also, the results confirmed the observed high percentage inhibition efficiency (%IE) of DB24C8.

Section (D): represents the surface analysis of different types of stainless steel using x-ray photoelectron spectroscopic analysis (XPS). All results explained depending on the increase of carbon percentage and the decrease in chloride percentages on the surface of different types of stainless steel. Also, the data gathered are in agreement with the above mentioned trend achieved from all the above applied techniques.

Section (E): represents the use of quantum chemical calculations for the study of corrosion inhibitors. It is evident that, the inhibition efficiency increases with increasing the energy of the highest occupied molecular orbital (HOMO) and with the ease of ionization of the molecule, which means that the inhibitor acts as an electron donor when blocking the corrosion reaction sites. Also, the results showed that the energies of (HOMO) of crown ethers decrease in the order:

DB24C8 > Kry-222 > Kry-22DD > DB18C6

This is in a good agreement with the previously mentioned experimental data obtained from the other applied techniques.

Section (F): represents the general discussion of the results obtained in this work through two important points which are:

- The effect of alloying elements present in stainless steels explain the dissolution of the investigated types of SS which obey this trend:
  430SS > 304SS > 316SS
- The effect of chemical structure of crown ethers on the corrosion inhibition of SS to discuss the arrangement of crown ethers according to their inhibition efficiencies on the dissolution of SS which obey this sequence:
  DB24C8 > Kry-222 > Kry-22DD > DB18C6

It was concluded that the type and number of active sites in crown ethers explain the above mentioned trend of crown ethers. Also, it was found that the alloying elements such as Cr, Ni and Mo play an important role in the corrosion resistance of stainless steels.