
The inhibitive effect of some rare earth elements on iron corrosion in clear and polluted sodium chloride solutions

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The thesis deals with studying the corrosion and corrosion inhibition of iron in clear and polluted 3.5% NaCl using some lanthanide chlorides. The thesis comprises three main chapters; In chapter I, an introduction is given which deals with the following fields of interest: 1. What is corrosion? 2. Chemistry of corrosion 3. Corrosion inhibitors 4. Techniques used in corrosion measurement 5. Examination of the surface 6. Literature survey on corrosion inhibition of lanthanide salts 7. The aim of the present work. In chapter II, the experimental techniques are given which deal with: 1. Materials and solution 2. Electrode preparation 3. Apparatus and techniques used for corrosion measurements Chapter III; is concerned with results and discussion. This chapter comprises the following: 1. The results obtained from potentiodynamic measurements The extrapolation of anodic / or cathodic Tafel lines gives the corrosion current density, i_{corr} , at the corrosion potential E_{corr} . This method is based on the electrochemical theory of corrosion processes developed by Wagner and Traud. Anodic and cathodic Tafel constants were determined from the slopes of the Tafel plots. On increasing the concentration of the inhibitor in the medium, the corrosion current is decreased. This indicates that the presence of the inhibitors in the medium retards the corrosion of iron in clear and polluted 3.5% NaCl and the extent of inhibition of corrosion depends on the concentration and the molecular structure of the inhibitor compounds. The rate of corrosion is decreased by increasing the concentration of the additives. This indicates that the presence of these additives in the medium retards the corrosion of iron in clear and polluted 3.5% NaCl. The degree of surface coverage (θ) for the inhibitors on iron surface increases with increasing the inhibitor concentration in the corrosive media. Application of Langmuir adsorption isotherm gives straight lines with slopes very closed to one. The effect of temperature on the inhibition efficiency was investigated for lanthanides compounds at 200 ppm and at temperature range 25-55°C. The inhibition efficiency decreases by rising the temperature from 25-55°C. The presence of inhibitors increases its activation energy. The inhibition was occurred through physical adsorption of the additives on iron surface. Thermodynamic parameters were calculated in the absence and presence of 200 ppm of lanthanide compounds. The addition of different concentrations of lanthanide compounds to clear and polluted 3.5% NaCl solution increases the breakdown potential towards more positive values, i.e. inhibits pitting corrosion of the iron. The relation between

pitting potential; Epit and the inhibitor concentrations for corrosion of iron in clear and polluted 3.5% NaCl solution, gives straight lines.² The results obtained from electrochemical impedance spectroscopy (EIS) measurements Nyquist and Bode plots of iron in uninhibited and inhibited clear and polluted 3.5% NaCl solution containing various concentrations of lanthanide compounds are plotted. the Nyquist plots are not perfect semicircles as expected from the theory of EIS and this difference can be explained as follows: This behavior can be attributed to the frequency dispersion as a result of roughness and in homogeneity of the electrode surface. Increase in the diameters of the semicircles with the concentration of the additives indicates that an increase in the protective properties of the iron surface. Thus, the capacitive semicircle is correlated with the dielectric properties and the thickness of barrier adsorbed film. Impedance parameters, such as, charge transfer resistance R_{ct} , and the double layer capacitance C_{dl} are derived from the Nyquist plots are determined for iron in clear and polluted 3.5% NaCl solution . The values of R_{ct} increase with increasing the concentration of the inhibitors and this in turn leads to a decrease in corrosion rate of iron. The decrease in values of double layer capacitance; C_{dl} can result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, In Bode plots the slope of $\log Z$ vs. $\log f$ relation should be -1. The high frequency limit corresponds to the solution resistance $R_s(R_\infty)$, while the lower frequency limit represents the sum of $R_s + R_{ct}$ where R_{ct} . The values of R_t and R_s calculated from Nyquist and Bode plots are in good agreement.³ The results obtained from electrochemical frequency modulation (EFM) measurements Inter modulation Spectrum for iron metal in clear and polluted 3.5% NaCl in the absence and presence of different concentrations of lanthanide chlorides compounds are studied. The harmonic and inter modulation peaks are clearly visible and are much larger than background noise. The corrosion parameters such as inhibition efficiency (% I), corrosion current density (i_{corr}), Tafel constants (β_a and β_c) and causality factors; CF-2, CF-3, at different concentrations of lanthanides in clear and polluted 3.5% NaCl at 25 °C are calculated.⁴ Surface examinationsi. Scanning electron microscope (SEM) studiesThe SEM micrographs of the specimen surface after 48 h of immersion in clear and polluted 3.5% NaCl solution in the absence and presence of different concentrations of $SmCl_3$ as corrosion inhibitor are studied. In the blank micrograph, flakes showing corrosion products can be observed. However, no pits or cracks can be seen in the micrographs. On the other hand, for the iron surface which was inhibited with different concentrations of $SmCl_3$ for 48 h immersion. It can see that the flakes in the surface of specimens are reduced when compared with that of the micrograph of the blank. SEM micrographs of iron before and after immersion for 48 h in clear and polluted 3.5% NaCl solution with constant concentration of lanthanides are also studied.ii. Energy dispersive x-ray (EDX) studiesThe EDX spectra were used to determine the elements present on the surface of the iron after 48 h of exposure to the uninhibited and inhibited 3.5% clear and polluted NaCl solution. For inhibited solutions with different concentrations of $SmCl_3$ the spectra show an additional line, demonstrating the existence of Sm and the height of this line increases by increasing the concentration of $SmCl_3$. The EDX analysis of the three lanthanides at constant concentration is also studied. Presence of peaks related to La, Ce and Sm,

is observed, this revealed the presence of a protective film of lanthanides on iron surface. The height of the peak increases as follows: LaCl_3