Preparation of Some Cationic Surfactants from Local Raw Materials and Evaluation of their Efficiency as Corrosion Inhibitors in Petroleum Industry

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تحضير بعض مواد ذات نشاط سطحي كاتيونية من مواد أولية محلية وتقييم كفاءتها كمثبطات تآكل في مجال صناعة البترول

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In this work two fatty acids were used as a source of alkyl halides. Untraditionally tertiary amines were prepared by ethoxylation of aromatic and aliphatic fatty amines. These alkyl halide and tertiary amines were used to prepare twenty five cationic quaternary ammonium surfactants (QAS$_S$). Their chemical structures were characterized and they tested as corrosion inhibitors for carbon steel in 1M HCl solution. The corrosion inhibition efficiency was measured using, weight loss and potentiodynamic polarization methods. The inhibition efficiencies obtained from the two employed methods are nearly closed. From the obtained data it was found that, the inhibition efficiency increases with increasing the inhibitor concentration until the optimum one. Also, it was found that the inhibition efficiency of QASs which based on ethoxylated aromatic tertiary amine is greater than the obtained efficiencies by the QASs which based on ethoxylated aliphatic tertiary amines. The QASs based on alkyl halide C16 exhibited the maximum inhibition efficiency 98.8%. Adsorption of the inhibitors on the carbon steel surface was found to obey Langmuir's adsorption isotherm. The quantum chemical calculations were done for some selected quaternary ammonium compounds based on their chemical structures QL1,4,5 –QP3,4,5. The following quantum chemical indices such as the bond length, bond angle, charge density distribution, highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), energy gap ΔE = HOMO –LUMO , and dipole moment (u) were considered. The relation between these parameters and the inhibition efficiencies was explained on the light of the chemical structure of the used inhibitors. The surface morphology of carbon steel sample was investigated by scanning electron microscopy (SEM).

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Introduction

1.1 Corrosion Problem in the Oil Industry:

Most metal exist in nature as stable ores of oxides, carbonates or sulfides. Refining them to make them useful requires energy. Corrosion is simply nature’s way of reversing an unnatural process back to a lower energy state. Preventing corrosion is vital in every step in the production of oil and gas. Corrosion attacks every component at every stage in the life of every oil and gas filed.

Because it is almost impossible to prevent corrosion, it is becoming more apparent that controlling the corrosion rate may be the most economical solution.

Corrosion process can be defined as the **degradation** of a **material** due to a **reaction** with its environment. Degradation implies deterioration of physical properties of the material. This can be a weakening of the material due to a loss of cross-sectional area, it can be the shattering of a metal due to hydrogen embitter, or it can be the cracking of a polymer due to sunlight exposure. **Materials** can be metals, polymers (plastics, rubbers, etc.), ceramics (concrete, brick, etc.) or composites mechanical mixtures of two or more materials with different properties.

Corrosion is a complex process and it can takes place in various forms depending on the properties of the material and the corrosive environment. Uniform corrosion refers to homogenous dissolution of materials, such as the corrosion of carbon steels in acidic solutions. The corrosion rate is almost the same everywhere and the corrosion can be mentioned easily. Few accidents occur as a result of the uniform corrosion due to its predictability, although significant amount of materials is lost in the process. Non uniform corrosion, however, concerns the inhomogeneous deterioration due to the heterogeneities of the material or the environment. It consists of various forms of corrosion such as intergranular corrosion, selective corrosion and pitting corrosion.

Most corrosion of metals is electrochemical in nature composed of two half cell reactions, an anodic reaction and a cathodic reaction. The anodic reaction consisting in the transfer of metal ions from the lattice to the solution, while the cathodic reaction consumes electrons librated during the anodic reaction. There are three common cathodic reactions, oxygen reduction (fast), hydrogen evolution from neutral water (slow), and hydrogen evolution from acid (fast).***Thomas, J. G., et al., (1967***).

1.2 Electrochemical Nature of Steel Corrosion

Most metal corrosion occurs via electrochemical reactions at the interface between the metal and an electrolyte. Corrosion of metals requires the presence of two important processes: anodic and cathodic reactions.

In iron or steel corrosion, electrochemical reactions may take place as follows: at the anodic area

$$Fe \longrightarrow Fe^{2+} + 2e^{-} \qquad (1.1)$$

This reaction is rapid in most media, as shown by the lack of pronounced polarization when iron is made anode employing an external current. When iron corrodes, the rate is usually controlled by the cathodic reaction, which in general is much slower (cathodic control). The cathodic reaction is:

$$H^{+} + e^{-} \longrightarrow 1/2\ H_2 \qquad (1.2)$$

This reaction proceeds rapidly in acids, but slowly in alkaline or neutral aqueous media. ***Blomgren, E., et al., (1961***) The rate of hydrogen evolution at specific pH depends on the presence or absence of low hydrogen over potential and impurities in the metal. For pure iron the metal surface itself may provide sites of hydrogen evolution, hence high purity iron continues to corrode in acids but at a measurable lower rate than does the commercial iron.

The cathodic reaction can be accelerated by dissolved oxygen in accordance with the following reactions (a process called depolarization) ***H.H Uhling, (1971).***

$$2H^{+} + 1/2\,O_2 + 2\,e^{-} \longrightarrow H_2O$$

$$H_2O + 1/2O_2 + 2\,e^{-} \longrightarrow 2\,OH^{-} \qquad (1.3\ \&\ 1.4)$$

Although the overall anodic and cathodic reactions are those given in equations (1.1-1.4), it is usually considered that the equations take place in a series of steps, one of which is the rate determining step (RDS). The most widely accepted anodic scheme is that proposed by Kelly ***E. J. Kelly,(1965)*** and is practically applicable in acid solutions.

1.3 Types of Corrosion

1.3.1 General or Uniform Corrosion

Differences in electrical potential occur on the surface of a piece of metal due to small differences in chemical composition, amount of cold work, etc. These differences set up small corrosion cells each with an anode and cathode. Corrosion continues until the metal is consumed or the film of rust formed on the surface sets up a barrier to the electrolyte.

1.3.2 Pitting Corrosion

Pitting corrosion is a complex but an important problem that is at the root of many corrosion failures. In pitting corrosion the surface of the metal is attacked in small localized areas. Organisms in water or breaks in a passive film can initiate corrosion. In pitting corrosion very little metal is removed from the surface but the effect is marked.

In passivated metals, or alloys that are exposed to solutions containing aggressive anions, primarily chloride, pitting corrosion results in local dissolution leading to the formation of cavities or (holes). The shape of the pits or cavities can vary from shallow to cylindrical holes, and the cavity is approximately hemispherical ***D.J. McAdam and G.W.Gell,(1928)***. The pit morphology depends on the metallurgy of the alloy chemistry of the environment as well as, on the leading conditions. As observed first by Mc. Adam ***D.J. McAdam and G.W.Gell,(1928)***, these pits may cause local increase in stress concentration and cracks may nucleate from them.

Pitting corrosion occurs mostly in solutions containing halides or oxyhalides, chlorides, bromides and hypochlorites are the most aggressive anions ***H.P. Leckie and H.H. Uhlig,(1966)***. Fluoride, iodide and iodine containing anions were thought to be without pitting tendency. However, iodide ions were found to cause pitting corrosion in many cases ***J.F. Marko,et.al.,(1991)***. Solutions of certain oxidizing actions produce the worst pitting reagents. The non - oxidizing metal halides such as Al, Ca and Na cause pitting to a lesser degree.

Electrochemical studies of pitting corrosion have found that there exists characteristic potentials. Stable pits, form at potentials noble to the pitting potential, E_{Pit}, and will grow at potentials noble to the repassivation potential, E_R, which is lower than E_{Pit}. During upward scanning in a cyclic polarization experiment, a stable pit starts growing at E_{Pit} where, the current increases sharply from the passive current level and, upon reversal of the scan direction, repassivates at E_R where the current drops back. It is generally considered that materials exhibiting higher values of E_{Pit} and E_R are more resistant to pitting corrosion, and cyclic-polarization experiments are commonly used for this purpose.

Pitting is considered to be autocatalytic in nature; once a pit starts to grow, the conditions developed are such that further pit growth is promoted. The anodic and cathodic electrochemical reactions that comprise corrosion separate spatially during pitting. The local pit environment becomes depleted in cathodic reaction (e.g. oxygen), which shifts most of the cathodic reaction to the boldly exposed surface where this reactant is more plentiful. The pit environment becomes enriched in metal cations and an anionic species such as chloride, which electromigrates into the pit to maintain charge neutrality by balancing the charge associated with the cation concentration. The pH in the pit is lower owing to cation hydrolysis and the absence of a local cathodic reaction. They tend to propagate the pit growth.

1.3.3 Stress Corrosion Cracking

Failure is due to the simultaneous influence of static tensile stresses and a corrosive environment and this is specific to a particular metal. The stresses may be internal such as those caused by cold work, welding, heat treatment or external forces caused by mechanical stresses set up by assembly practices. A good example of this form of corrosion is 316 stainless steel in marine environments. 316 stainless steel was developed to withstand attacks in chloride environments, but if stressed the steel will fail by stress corrosion cracking.

1.3.4 Intergranular Corrosion

Corrosion occurs at the grain boundaries due to a difference in potential between the anodic grain boundaries and the cathodic grains. "Sensitized" stainless steels, where carbides have been precipitated in the grain boundaries during heat treatment or in the heat- affected zone of a weld, are particularly susceptible to intergranular corrosion.

1.3.5 Corrosion Fatigue

Is a failure under repeated cycling stresses in a corrosive environment.

1.3.6 Filiform Corrosion

Filiform corrosion appears as a network of corrosion trials, of a worm like structure, particularly beneath thin organic salts containing chlorides, which have been left on the surface prior to coating, are suspected.

1.3.7 Crevice Corrosion

Crevice corrosion occurs when there is a difference in ion, or oxygen, concentration between the metal and its surroundings. Oxygen starvation in an electrolyte at the bottom of a sharp V-section will set up an anodic site in the metal that then corrodes rapidly.

1.3.8 Galvanic or bi- Metallic Corrosion

Galvanic corrosion takes place between two different metals, or coatings, which are joined together in the presence of an electrolyte. Each metal has a potential different from any other metal when placed in an electrolyte. A series can be built up of all the metals relative to each other.

1.3.9 Fretting Corrosion

Fretting corrosion occurs when two or more parts rub against each other. The rubbing action removes the corrosion products and exposes new metal to the electrolyte.

1.3.10 Erosion Corrosion

Erosion is the removal of metal by the movement of fluids against the surface. The combination of erosion and corrosion can provide a severe rate of corrosion.

1.3.11 Selective Leaching or Demetalification

Demetalification is the removal of one of the alloying elements in an alloy by the electrolyte. This results in a " spongy" metal. Typical example is the removal of zinc in chloride waters form brass (dezincification).

1.4 Corrosion Prevention By Electrochemical Methods

1.4.1 Cathodic Protection :

Cathodic protection is an electrochemical means of corrosion in which the oxidation reaction in a galvanic cell is concentrated at the anode and suppresses corrosion of the cathode in the same cell. For example, the steel pipeline is cathodically protected by its connection to a sacrificial magnesium anode buried in the same soil electrolyte. Cathodic protection is different from anodic protection. In cathodic protection, the object to be protected is the cathode, but in anodic protection, the object to be protected is the anode. Anodic protection can be used on only a limited number of alloys in certain restricted environment, but cathodic protection can, in principle, be applied to any metal. In practice, cathodic protection is primarily used on carbon steel. The effectiveness of cathodic protection allows carbon steel, which has a little natural corrosion resistance, to be used in such corrosive environments as sea water, acid soils, salt-laden concrete, and many other corrosive environments. Properly designed and maintained cathodic protection system can prevent corrosion indefinitely in these environments.

1.4.2 Anodic Protection

The term anodic protection refers to corrosion protection achieved by maintaining an active- passive metal or alloy in the passive region by an externally applied anodic current. Solution oxidizing power and corrosion potential are equivalent, and therefore it is possible to achieve passivity by altering the potential of the metal by an appropriate external power supply. Since the potential must be maintained within the passive region, it is necessary to use a special device called a potentiostat which is capable of maintaining a constant electrode potential by controlling the anodic current.

1.5 Corrosion Inhibitors

Corrosion products are formed when a metal gives its electrons to the oxidizing substances. Formation of an oxide of iron due to oxidation of the iron atoms is a well-known example of electrochemical corrosion. This type of damage typically produces oxides and/or salts of the original metal. Corrosion can be concentrated locally to form a pit or crack, or it can extend across a wide area more or less uniformly corroding the surface. This can be delayed through protection or inhibition methods to reduce the activity of these surfaces by, for example, painting the metal. Another way of protecting these metals from corrosion is to use corrosion inhibitors.

An inhibitor is a chemical substance which, when added in small concentrations to corrosive environment effectively decreases or prevents the reaction of the metal with the environment ***C.M. Mustafa and S.I. Dulal,(1996)***. Inhibitors often work by adsorption on the metallic surface and protect it by forming an isolating film ***B. M. Praveen et al., (2009),***