

# ***CHAPTER (1)***

## ***INTRODUCTION***

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### **1. INTRODUCTION**

#### **1.1. Nanoscience as a New Trend**

Nanotechnology, shortened to "Nanotech", is the study of the control of matter on an atomic and molecular scale. Generally nanotechnology deals with structures of the size 100 nanometers or smaller, and involves developing materials or devices within that size. Nanotechnology is very diverse, ranging from novel extensions of conventional device physics, to completely new approaches based upon molecular self-assembly, to developing new materials with dimensions on the nanoscale, even to speculation on whether we can directly control matter on the atomic scale.

There has been much debate on the future of implications of nanotechnology. Nanotechnology has the potential to create many new materials and devices with wide-ranging applications, such as in medicine, electronics, and energy production. On the other hand, nanotechnology raises many of the same issues as with any introduction of new technology, including concerns about the toxicity and environmental impact of nanomaterials [Buzea et al., 2007], and their potential effects on global economics, as well as speculation about various doomsday scenarios. These concerns have led to a debate among advocacy groups and governments on whether special regulation of nanotechnology is warranted.

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## 1.2. Metal Nanoparticles

Colloidal particles are increasingly receiving attention as important starting points for the generation of micro and nanostructures [Yakutik et al., 2004]. These particles are under active research because they possess interesting physical properties differing considerably from that of the bulk phase. It comes from small sizes and high surface/volume ratio [Patel et al., 2005].

Nanoparticles are commonly defined as particles less than 100 nm in diameter [Ichinose et al., 1992, El-Shall and Edelstein, 1996]. Due to this small size, nanoparticles have a large fraction of surface atoms, i.e. a high surface to volume ratio. This increases the surface energy compared with that of bulk material. The high surface to volume ratio together with size effects (quantum effects) gives nanoparticles distinctively different properties (chemical, electronic, optical, magnetic and mechanical) from those of bulk material. For instance, nanoparticle-based semiconductor sensors exhibit higher sensitivities to air pollutants and have lower detection thresholds and lower operating temperatures [Baraton and Merhari, 2004]. In various applications e.g. electronic, magnetic and optical [Kruis et al., 1998], in bioanalysis [Penn et al., 2003] and in environmental remediation [Kamat and Meisel, 2003, Zhang, 2003], nanoparticles are used.

In recent years, nanoparticle research has become a subject of intense interest in the fields of science and technology. This is evident from the rapid increase in the number of publications in the field of nanomaterials, in particular in the area of synthesis of nanoparticles and their self-assembly. Metal nanoparticles are finding new applications in

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fields such as nanoelectronics, non-linear optics, biophysics, catalysis, etc.

Metal nanoparticles can be synthesized through physical and chemical methods. In physical methods, particles are prepared by physical processes like laser ablation, evaporation and condensation, ion sputtering, etc. In chemical methods, nanoparticles are prepared by chemical oxidation, reduction, etc. of the precursor material under controlled reaction conditions. The chemical methods of synthesis score over physical methods in terms of energy efficiency.

Metallic nanostructures have been studied extensively and are emerging as important colorimetric reporters due to their high extinction coefficients, which are typically several orders of magnitude larger than those of organic dyes. In particular, nanostructures made from the noble metals, such as those of silver or gold, with their associated strong Plasmon resonance, have generated great interest [Kadir et al., 2004].

### **1.2.1. Applications of Metal Nanoparticles**

Nanoparticles have become a part of our daily life, in the form of cosmetics [Perugini et al., 2002], drug delivery systems [Jin and Ye 2007], therapeutics [Czupryna and Tsourkas, 2006] and biosensors [Prow et al., 2006].

Metal colloidal nanoparticles are becoming increasingly important in a variety of scientific fields. In molecular spectroscopy applications, the interest stems from the significant improvement in the detection of the Raman signal from molecules adsorbed on roughened metal surfaces. In

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the field of surface-enhanced Raman scattering (SERS), [Fleischmann et al., 1974] the spectral signature from single molecules has recently been observed [Nie and Emory, 1997, Kneipp et al., 1997]. This effect is believed to be due to the significant electromagnetic field enhancement at the metal particle surface that strongly interacts with the internal energy levels of the adsorbed molecule [Moskovits, 1985]. The Plasmon resonance unique colors! and the large effective scattering cross section of individual silver nanoparticles, as well as their non bleaching properties have significant potential for single molecule labeling based biological assays [Schultz et al., 2000, 1999]. Metal nanoparticles are also used in various near field optical microscopy applications [Silva et al., 1994, Sqalli et al., 2000] where they provide increased signal output due to their efficient scattering properties.

### 1.2.2. Silver Nanoparticles

In recent years, noble metal nanoparticles have been extensively studied and various approaches have been employed for the preparation of metal nanoparticles [Yin et al., 2003, Penner , 2002, Raveendran et al., 2003, Lin et al., 2003]. Research on metal colloids is greatly stimulated due to the unique properties of nanoscopic materials in optical properties, catalytic activity, and magnetic properties which are different from bulk metals. Many studies on metal colloids have been reported in particular for silver, gold, and copper colloids. Among the noble metal nanoparticles, silver nanoparticles have attracted more attention [Jiang et al., 2005, Evanoff et al., 2004] for their advantage on various studies such as photosensitive components [Hailstone, 1995], catalysts [Shiraishi and Toshima, 1999, Sclafani et al., 1991], and surface-enhanced Raman spectroscopy.

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Silver nanoparticles have been found to have strong anti-microbial activity, because of which they are used in wound dressings, contraceptive devices, surgical instruments and bone prostheses [Kowshik et al., 2003, Cho et al., 2005, Mukherjee et al., 2001, Duran et al., 2005] and also coated on the ocular lens for the prevention microbial activity [Alt et al., 2004]. Moreover silver nanoparticles are reported to posse's anti-fungal activity, anti - inflammatory effect [Nadworny et al., 2008] and anti-viral activity [Rogers et al., 2008]. Silver nanoparticles could be well applied in therapy when the effects of silver nanoparticles are completely understood.

Investigation of the optical properties of silver nanoparticles is very interesting since the silver nanoparticles strongly absorb in the visible region due to surface plasmon resonance [Kapoor, 1998].

Silver nanoparticles exhibit new optical properties, which are not observed neither in molecules nor in bulk metals. One example is presence of absorption band in visible light region. This band appears due to the surface-Plasmon- oscillation modes of conduction electrons which are coupled through the surface to external electromagnetic fields [Stepanov, 2005]. The surface Plasmon resonance and large effective scattering cross section of individual silver nanoparticles make them ideal candidates for molecular labeling, where phenomena such as surface enhance Raman scattering (SERS) can be exploited [Wei et al., 2005]. In addition, silver nanoparticles have recently been shown to be a promising antimicrobial material [Jain and Pradeep, 2005]

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### 1.2.2.1. Preparation of Silver Nanoparticles

A number of methods have been developed for preparing metal colloids, such as radiation chemical reduction, chemical reduction with or without stabilizing polymers, chemical or photoreduction in reverse micelles and thermal decomposition in organic solvents [Hoon et al., 2001].

Metallic silver colloids were first prepared more than a century ago. Silver nanoparticles can be synthesized using various methods: chemical, electrochemical [Vorobyova et al., 1999],  $\gamma$ -radiation [Choi et al., 2005] photochemical [Li et al., 2005], laser ablation [Tsuji et al., 2003] etc. The most popular preparation of silver colloids is chemical reduction of silver salts by sodium borohydride or sodium citrate. This preparation is simple, but the great care must be exercised to make stable and reproducible colloid. The purity of water and reagents, cleanliness of the glassware are critical parameters. Solution temperature, concentrations of the metal salt and reducing agent; reaction time influences particle size. Controlling size and shape of metal nanoparticles remains a challenge [Bell and Myrick, 2001]. The size-induced properties of nanoparticles enable the development of new applications or the addition of flexibility to existing systems in many areas, such as catalysis, optics, microelectronics and so on.

### 1.3. Self Assembling of thiols on metal nanoparticles

Recent years have witnessed an exponential growth in fundamental and applied studies of metal nanoparticles with size- and shape-dependent

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properties [Roduner, 2006]. Much of this has been propelled by readily available methods of surface functionalization, in particular by the chemisorption of organic thiols on gold to produce monolayer-protected nanoparticles [Love et al., 2005].

Ironically, the benefits (and limitations) of organic surface functionalization may have also contributed toward a dichotomy in nanoparticle research as a function of particle size. Alkanethiol-passivated gold nanoparticles are typically prepared in the 2–10 nm size range by the reduction of gold chloride in the presence of the surfactant, such as the popular two-phase protocol first introduced by Brust et al. [1994]. Nanoparticles of this size can be readily dispersed in organic or aqueous solvents, depending largely on the terminal groups of the chemisorptive monolayer. On the other hand, colloidal gold nanoparticles (10 nm), which are stabilized electrostatically in aqueous dispersions, are susceptible to kinetic aggregation upon treatment with simple alkanethiols regardless of their interfacial surface properties [Weisbecker et al., 1996]. Dispersion control of these larger metal nanoparticles is important for their subsequent application as functional nanostructures; for example, gold and silver nanostructures are well known for their size-dependent optical resonances generated by localized surface plasmons, which have been applied with great effect in numerous chemical and bioanalytical sensing modalities [Wei, 2004] as well as in nanophotonics [Kang et al., 2005]. The factors which determine dispersion stability or surfactant robustness are often overlooked or dismissed as simple colloidal processing issues, but these are in fact of fundamental importance to materials synthesis and fabrication methodologies, and remain critical bottlenecks in the development of functionalized nanomaterials [Balasubramanian et al., 2007].

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One of the major challenges is to control the size and monodispersity of metal nanoparticles, and to organize them into nanostructured devices and composite materials. Dispersing metal particles in organic solvents is appealing since the low interfacial energies should allow for a high degree of control during solution and surface processing. Thiols have been used to stabilize dispersions of metal nanoparticles in organic solvents, however studies on the spontaneous assemblies of organic thiols on the surface of gold nanopartilce to date have mainly relied on the availability of a relatively few commercially available unbranched alkanethiols **Schadt et al. [2006]** demonstrated that the size of gold nanoparticles can be tuned molecularly by manipulating different length alkanethiols. By using the commercially available alkanethiols  $C_NH_{2N+1}SH$  with  $N = 5$  to 17, gold nanoparticle sizes ranging from 5 to 8 nm with good monodispersity were obtained. An increase in the alkanethiol chain length leads to a gain in stabilization energy due to additional interchain cohesive interactions. In addition, gold nanoparticles below 5 nm are thought to be of great practical value for numerous applications [**Hussain et al., 2005**].

## **1.4. Surfactants and Their Classification**

### **1.4.1. Surface - Active Agents**

Surface active agents (usually referred to surfactants) are amphiphilic compounds, i.e., they have one part that has an affinity for non polar media and one part that has an affinity for polar media. Furthermore, it can be defined as molecules capable of associating to form micelles. These molecules oriented between phases lowering the surface or interfacial tension of medium in which they are dissolved.

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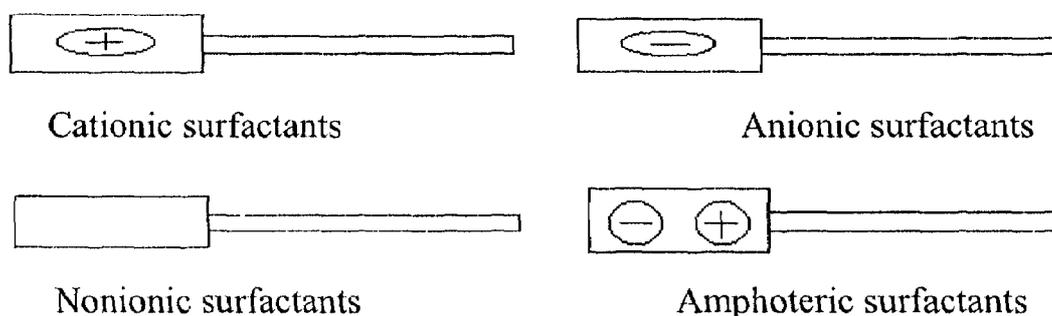


**Figure (1):** Shape of a surfactant

The unusual properties of aqueous surfactant solutions can be ascribed to the presence of hydrophilic head group and a hydrophobic chain (or tail) as in figure (1) in the molecule where the polar or ionic head group usually interacts strongly with an aqueous environment, in which case it is solvated via dipole – dipole or ion – dipole interactions

### 1.4.2. Classification of Surfactants

Surfactants are classified according to their polar head group into four main types; i.e., surfactants with a positively charged head group are referred to as cationic surfactants, where as anionic surfactants contain polar head groups with a negatively charge. Uncharged surfactants are generally referred to as non-ionic, and zwitterionic (Amphoteric) surfactants contain both a negatively charged and a positively charged head group as shown in schem.(1) [Martin, 2002].



schem (1): Schematic illustration of various types of surfactants.

### 1.4.2.1. Cationic Surfactants

Cationic surfactants are frequently based on amine-containing polar head groups. Due to their charged nature, the properties of cationic surfactants, e.g; surface activity or structure formation, are generally strongly dependent on the salt concentration, and on the valency of anions present. Cationic surfactants are generally water soluble when there is only one long alkyl group. They are generally compatible with most inorganic ions and hard water, but they are incompatible with metasilicates and highly condensed phosphates. They are also incompatible with protein-like materials. Cationic surfactants are generally stable to pH changes, both acid and alkaline. They are incompatible with most anionic surfactants, but they are compatible with non-ionics. These cationic surfactants are insoluble in hydrocarbon oils. In contrast, cationic surfactants with two or more long alkyl chains are soluble in hydrocarbon solvents, but they become only dispersible in water (sometimes forming bi-layer vesicle type structures).

The critical micelle concentration (CMC) of cationic surfactants is close to that of anionics with the same alkyl chain length [Tharwhat, 2005]. Cationic surfactants are frequently used as antibacterial agents, which may be advantageous also in certain drug delivery applications, such as delivery systems to the oral cavity. However, cationic surfactants are frequently also irritant and sometimes even toxic, and therefore their use in drug delivery is significantly more limited than that of non-ionic, zwitterionic, and anionic surfactants [Kwon and Kataoka, 1995].

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### 1.4.2.2. Anionic Surfactants

They are the most widely used class of surfactants in industrial applications due to their relatively low cost of manufacture, and they are used in practically every type of detergent. For optimum detergency the hydrophobic chain is a linear alkyl group with a chain length in the region of 12–16 carbon atoms. Linear chains are preferred since they are more effective and more degradable than branched ones. The most commonly used hydrophilic groups are carboxylates, sulfates, sulfonates and phosphates.

Several other anionic surfactants are commercially available such as sulfosuccinates, isethionates and taurates and these are sometimes used for special applications.

### 1.4.2.3. Non-ionic Surfactants

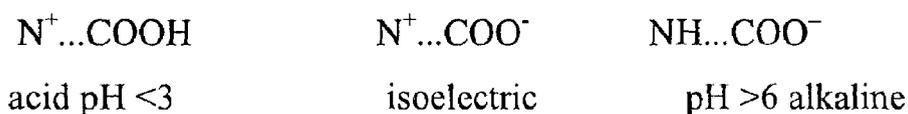
The most common non-ionic surfactants are those based on ethylene oxide, referred to as ethoxylated surfactants. Several classes can be distinguished: alcohol ethoxylates, alkyl phenol ethoxylates, fatty acid ethoxylates, monoalkylamide ethoxylates, sorbitan ester ethoxylates, fatty amine ethoxylates and ethylene oxide–propylene oxide copolymers (sometimes referred to as polymeric surfactants). Another important class of non-ionics is the multihydroxy products such as glycol esters, glycerol (& polyglycerol) esters, glucosides (& polyglucosides) and sucrose esters. Amine oxides and sulphinyl surfactants represent non-ionics with a small head group.

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They tend to be more effective than other surfactants for removal of oily soil from synthetic fabrics. Most non-ionics are considered low-foaming products, have good cold water solubility, and have a low critical micelle concentration, making them effective at low concentration. Their compatibility with cationic fabric softeners makes them preferable to anionics in certain formulations. They are more common in industrial applications than are anionics. The CMC of non-ionic surfactants is about two orders of magnitude lower than the corresponding anionics with the same alkyl chain length.

#### 1.4.2.4. Amphoteric (Zwitterionic) Surfactants

These are surfactants containing both cationic and anionic groups. The most common amphoteric are the N-alkyl betaines, which are derivatives of trimethyl glycine  $(\text{CH}_3)_3\text{N}^+\text{CH}_2\text{COO}^-$  (described as betaine). An example of betaine surfactant is lauryl amido propyl dimethyl betaine  $\text{C}_{12}\text{H}_{25}\text{CON}^+(\text{CH}_3)_2\text{CH}_2\text{COO}^-$ . These alkyl betaines are sometimes described as alkyl dimethyl glycinate. The main characteristic of amphoteric surfactants is their dependence on the pH of solution in which they are dissolved. In acid pH solutions, the molecule acquires a positive charge and behaves like a cationic surfactant, whereas in alkaline pH solutions they become negatively charged and behave like an anionic surfactant. A specific pH can be defined at which both ionic groups show equal ionization (the isoelectric point of molecule) (Scheme2).



Scheme (2) the isoelectric point of molecule

Amphoteric surfactants are sometimes referred to as zwitterionic molecules. They are soluble in water, but the solubility shows a minimum at the isoelectric point. Amphoterics show excellent compatibility with other surfactants, forming mixed micelles. They are chemically stable both in acids and alkalis. The surface activity of amphoterics varies widely and depends on the distance between the charged groups, showing maximum activity at the isoelectric point [Thomas, 2001].

## 1.5. POLYMERIC SURFACTANTS

Self-assembling polymers have been received considerable attention of synthetic and physical chemists who work on nano-scale structures, latex stabilizers, emulsifiers, biomedical and pharmaceutical applications [Liu et al., 2001, Uhrich et al., 1999]. Recently, polymer micelle is regarded as one of the most promising candidates for carrier of delivery bioactive materials such as water-insoluble drugs [Kabanov et al., 1995, Gohy et al., 2001], hormones [Kawashima et al., 1999, Brodbeck et al., 1999] and plasmid DNA [De Smedt et al., 2000, Jerasak et al., 2004]

Recently, there has been increasing interest in the synthesis and characteristics of polymeric surfactants, accounting for its diverse applications such as in enhanced oil recovery [Babadagli, 2003], polymer LB membrane [Kim et al., 2000] and emulsion polymerization [Riess, 1999]. Although necessarily less well-defined than small-molecule surfactants, polymeric surfactants probably offer greater opportunities in terms of flexibility, diversity and functionality [Liu and Armes, 2001, Bobin et al., 1999, Griffithsa and Stilbs, 2002]. Polymeric surfactant consists of both hydrophobic and hydrophilic

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groups, so it can also reduce the surface tension of aqueous phase, stabilize monomer droplets or polymer particles and can form aggregates as the results of intermolecular and/or intramolecular hydrophobic interactions [Wang et al., 2006].

Polyaniline (PANI) is one of the promising conducting polymers because of its conductivity reversible redox characteristics, electrochromic behavior and environmental stability in air. The properties inbuilt in PANI provide potential applications in rechargeable batteries [Wang et al., 2007, Ghanbari et al., 2006], biosensor [Zou et al., 2007], electrochromic device [Gerlache et al., 1998, Hu et al., 2007], photoelectrochemical cell [Maia et al., 1999, Huang et al., 2001] and corrosion protection [Rokovic et al., 2007]. However, PANI does not show electroactivity at less acidic conditions and this limits its applications in biosensor. It becomes necessary to prepare derivatives of PANI having the required properties to use in biochemical applications.

In recent years, a great deal of attention has been paid on the synthesis of aniline-based copolymers. This becomes necessary due to the fact that it is difficult to synthesize new PANI derivatives with electrical properties and stability better than PANI. Simultaneous polymerization of aniline and other aniline derivatives offers the possibility to prepare copolymers of aniline. These copolymers retain the properties of PANI with additional newer properties. Copolymerization of aniline with another aniline derivative can be performed using chemical and electrochemical methods [Márquez et al., 2007, Chen et al., 2002, Gemeay et al., 2007]. Aniline-based copolymers exhibit pH dependent electrical properties and could be used as sensors.

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## 1.6. Thiols as a Special Subclass of Surfactants

The chemical reactivity of thiol surfactants make it different from other surfactants. They associate specifically with transition metals to form metal chalcogenides. Although alkanethiols are used most commonly in the synthesis of gold monolayer protected clusters (MPCs), [Daniel and Astruc, 2004] they are also used in the formation of nanoparticles of many other materials. For gold nanoclusters, the assembly of thiols on their surfaces also can be accompanied by metal etching processes [Prasad et al., 2002]. One of the most common routes to gold nanoparticles functionalized with thiols is the Brust-Schiffrin method. The thiols in this reaction and other related routes are involved in the reduction of gold precursor salts to a Au (I)-thiol polymer [Yee et al., 1999, Chen et al., 2000].

The Au (I)-thiol intermediates are also useful for forming bimetallic nanoparticles (Au-Pd, Au-Cu, and Au-Ag) via galvanic exchange reactions with thiol-protected metallic nanoparticles. [Song et al., 2003] If dithiols, such as dimercaptosuccinic acid, are used instead of monothiols, Au (III) is reduced completely to Au (0), eliminating the need for any additional reductants in the formation of small (1-2 nm) gold nanoparticles [Negishi and Tsukuda, 2003].

The ratio of alkanethiol to Au (III) controls the size of the resulting nanoparticles by adjusting the relative rates of particle nucleation and growth (higher ratios yield smaller particles) [Chen et al., 1999]. Methods of forming gold nanoparticles in the presence of thiols can only be used to form small (< 5 nm in diameter) particles. The formation of particles with diameters > 5 nm requires the use of surfactants that have a

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faster desorption rate than thiols (e.g., phosphines and cetyltrimethylammonium bromide (CTAB) or stabilization by electrostatic charges (citric acid synthesis) [Jana et al., 2001]. These larger particles can be functionalized with thiols via “ligand-exchange” methods to displace the weakly bound surfactants.

## **1.7. Corrosion and Corrosion Inhibitors**

### **1.7.1. Definition of Corrosion**

The word corrosion stands for material or metal deterioration or surface damage in an aggressive environment. Corrosion is a chemical or electrochemical oxidation process, in which the metal transfers electrons to the environment and undergoes a valence change from zero to a positive value. The environment may be a liquid, gas or hybrid soil-liquid. These environments are called electrolytes since they have their own conductivity for electron transfer.

An electrolyte is analogous to a conductive solution, which contains positively and negatively charged ions called cations and anions, respectively. An ion is an atom that has lost or gained one or more outer electron (e) and carries an electrical charge. Thus, the corrosion process which can be chemical in nature or electrochemical due to a current flow requires at least two reactions that must occur in a particular corrosive environment. These reactions are classified as anodic and cathodic reactions and are defined below for a metal (M) immersed in acidic solution. Hence, metal oxidation occurs through an anodic reaction and reduction is through a cathodic reaction as shown.

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where  $M$  = metal

$M^{+z}$  = metal cation

$H^{+}$  = hydrogen cation

$Z$  = valance oxidation state

The interpretation of the above equations indicates that an anodic reaction, which is equivalent to what is known as oxidation, loses metal electrons and the cathodic reaction accepts or gains electrons for reducing pertinent ions [Perez, 2004]. Consequently, both anodic and cathodic reactions are coupled in a corrosion process. Adding eqs (1) and (2) yields eq. (3) thus, REDOX (RED = reduction and OX = oxidation) is the resultant reaction equation, eq. (3), and represents the overall reaction at equilibrium where the anodic and cathodic reaction rates are equal. Observe that the anodic reaction is also referred to as an oxidation reaction since it has lost electrons, which has been gained by the cathodic reaction. Thus; a cathodic reaction is equivalent to a reduction reaction.

## 1.7.2. Corrosion Types

There is not a unique classification of the corrosion types, but the following classification is the more acceptable.

### 1.7.2.1. General Corrosion

This is the case when the exposed metal/alloy surface area is entirely corroded in an environment such as a liquid electrolyte (chemical solution, liquid metal), gaseous electrolyte (air, CO<sub>2</sub> and SO<sub>2</sub> etc.), or a hybrid electrolyte (solid and water, biological organisms, etc.). Some

types of general corrosion and their description are given below [Pohlman, 1987].

- Atmospheric Corrosion on steel tanks, steel containers, parts, Aluminum plates, etc.
- Galvanic Corrosion between dissimilar metal/alloys or microstructural phases (pearlitic steels, copper alloys and lead alloys)
- High temperature corrosion on carburized steels that forms a porous scale of several iron oxide
- phases Liquid metal corrosion on stainless steel exposed to a sodium chloride (NaCl) environment
- Molten salt corrosion on stainless steels due to molten fluorides (LiF and BeF<sub>2</sub>)
- Biological corrosion on steel.

#### 1.7.2.2. Localized Corrosion

This term implies that specific parts of an exposed surface area corrode in a suitable electrolyte. This form of corrosion is more difficult to control than general corrosion. Localized corrosion can be classified as following

- Crevice corrosion which is associated with a stagnant electrolyte such as dirt, corrosion product, sand, etc. It occurs on metal/alloy surface holes, underneath a gasket, lap joints under bolts, under rivet heads.
  - Filiform corrosion is basically a special type of crevice corrosion, which occurs under a protective film. It is common on food and beverage cans being exposed to the atmosphere.
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- Pitting corrosion is an extremely localized corrosion mechanism that causes destructive pits.
- Oral corrosion occurs on dental alloys exposed to saliva.
- Biological corrosion due to fouling organisms non-uniformly adhered on steel in marine environments.
- Selective leaching corrosion is a metal removal process from the base alloy matrix, such as dezincification (Zn is removed) in alloys and graphitization (Fe is removed) in cast irons.

### 1.7.3. The Method Used for Corrosion Studies

There are different techniques which can be used to determine the corrosion rate.

#### 1.7.3.1. Weight Loss

- (a)-Directly by measuring the loss of weight sample due to its corrosion
- (b)-Indirectly by monitoring the free ion in solution ( $\text{Fe}_2\text{O}_4$ ) by titrating it against  $\text{K}_2\text{Cr}_2\text{O}_7$

#### 1.7.3.2. Gasometry

In most corrosion processes either ( $\text{H}_2$ ) or ( $\text{O}_2$ ) is evolved and can be used as measure for corrosion. It is generally detected by collecting the gas over aqueous solution and the volume of the collected gases read directly.

#### 1.7.3.3. Polarization Technique

The polarization resistance ( $R_p$ ) of a metal/electrolyte system and the pitting or breakdown potential ( $E_b$ ) can be determined using at least

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two-electrode system [Fontana, 1986]. Subsequently, the rate of metal dissolution or corrosion rate is calculated using a function of the form equation 4 as following

$$i_{\text{corr}} = f(\beta, R_p) \cdot i_0 \quad (4)$$

### a) Linear Polarization

The linear polarization is confined to a small magnitude of the overpotentials  $\eta_a$  and  $\eta_c$  respectively, using linear coordinates. This technique allows the determination of  $i_{\text{corr}}$  using a potential range of  $\pm 10$  mV from the  $E_{\text{corr}}$  [Shoesmith, 1987]. Prior to determining the polarization resistance is estimated from the linear slope of the curve as shown in equation 5

$$R_p = \Delta E / \Delta i \quad (5)$$

### b) Tafel Extrapolation

This method involves the determination of the Tafel slopes  $b_a$  and  $b_c$  as well as  $E_{\text{corr}}$  and  $i_{\text{corr}}$  from a single polarization curve. This curve is known as the Stern diagram (non-linear polarization). This non-linear curve is divided into two parts. If  $E > E_0$  the upper curve represents an anodic polarization behavior for oxidation of the metal M. On the contrary, if  $E < E_0$  the lower curve is a cathodic polarization for hydrogen reduction as molecular gas (hydrogen evolution). Both polarization cases deviate from the electrochemical equilibrium potential ( $E_{\text{corr}}$ ) due to the generation of anodic and cathodic overpotentials [Pourbaix, 1973].

Both anodic and cathodic polarization curves exhibit small linear parts known as Tafel lines, which are used for determining the Tafel slopes  $b_a$  and  $b_c$  diagram. These slopes can be determined using either the Evans or Stern diagram.

Extrapolating the Tafel or Evans straight lines until they intersect define the  $E_{\text{corr}}$ ,  $i_{\text{corr}}$  point.

#### 1.7.3.4. Electrochemical Impedance Spectroscopy

The electrochemical impedance spectroscopy (EIS) technique is very useful in characterizing an electrode corrosion behavior. The electrode characterization includes the determination of the polarization resistance ( $R_p$ ) corrosion rate and electrochemical mechanism [McDonald, 1978, Mansfeld, 1982, Wang et al., 1996, Law et al., 2000]. The usefulness of this method permits the analysis of the alternating current (AC) impedance data, which is based on modeling corrosion process by an electrical circuit. Several review papers address the electrochemical impedance technique based on the alternating current (AC) circuit theory [Mansfeld, 1981, Scully, 1999, McDonald and McKubre, 1982, Hladky et al., 1980].

#### 1.7.4. Corrosion Inhibitors

Corrosion of metallic surfaces can be reduced or controlled by the addition of chemical compounds to the corrodent. This corrosion control is called inhibition and the compounds added are known as corrosion inhibitors. These inhibitors will reduce the rate of either anodic oxidation or cathodic reduction, or both. The inhibitors themselves form a protective film on the surface of the metal. It has been postulated that the inhibitors are adsorbed into the metal surface either by physical (electrostatic) adsorption or chemisorption [Trabanelli and Carassiti, 1970, Foroulis, 1969, Riggs, 1973, Thomas, 1976].

Physical adsorption is the result of electrostatic attractive forces between the organic ions and the electrically charged metal surface.

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Chemosorption is the transfer, or sharing of the inhibitor molecule's charge to the metal surface, forming a coordinate-type bond. The adsorbed inhibitor reduces the corrosion rate of the metal surface either by retarding the anodic dissolution reaction of the metal by the cathodic evolution of hydrogen, or both. Inhibitors can be used at pH values of acid from near neutral to alkaline. They can be classified in many different ways according to

1. Their chemical nature (organic or inorganic substances)
2. Their characteristics (oxidizing or nonoxidizing compounds)
3. Their technical field of application (pickling, descaling, acid cleaning, cooling water systems, and the like)

### **1.7.5. Classification of Inhibitors**

Inhibitors can be classified in several ways as previously indicated.

The inhibitors will be classified as following:

1. Passivation inhibitors
2. Organic inhibitors
3. Precipitation inhibitors

#### **1.7.5.1. Passivation Inhibitors**

Passivation inhibitors are chemical oxidizing materials such as chromate  $K_2Cr_2O_7$  and nitrite  $KNO_2$  or substances such as  $Na_3PO_4$  or  $NaBrO_7$ . These materials favor adsorption on the metal surface of dissolved oxygen. This is the most effective and, consequently, the most widely used type of inhibitor [Putflova et al., 1964].

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### 1.7.5.2. Organic Inhibitors

These materials build up a protective film of adsorbed molecules on the metal surface that provide a barrier to the dissolution of the metal in the electrolyte. Since the metal surface [Podobaev et al., 1967].

Organic compounds constitute a broad class of corrosion inhibitors which cannot be designed specifically as anodic, cathodic. Anodic and cathodic effects alone are sometimes observed in the affect the entire surface of a corroding metal when present in sufficient Concentration both anodic and cathodic areas probably are inhibited, but to varying degrees on the potential of the metal, chemical structure of the inhibitor molecule, and size of the molecule. The inhibitor is the result of adsorption on the metal surface. The film formed by adsorption of soluble organic inhibitors is invisible.

Organic inhibitors will be adsorbed according to the ionic charge of the inhibitor and the charge on the metal surface. Cationic inhibitors (positively charged) such as amines, or anionic inhibitors (negatively charged), such as sulphonate will be adsorbed preferentially, depending on whether the metal is charged negatively or positively (opposite sign charges attract). The in-between potential at which neither cationic nor anionic molecules are preferred is known as the zero point of charge or ZPC. Thus, a combination of cathodic protection and an inhibitor which is adsorbed more strongly at negative potentials gives greater inhibition than either cathodic protection or an inhibitor when used alone.

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### 1.7.5.3. Precipitation inhibitors

Precipitation inhibitors are compounds that cause the formation of precipitates on the surface of the metal, thereby, providing a protective film. Hard water that is high in calcium and magnesium is less corrosive than soft water because of the tendency of the salts in the hard water to precipitate on the surface of the metal and form a protective film.

### 1.7.6. Using of nanoparticle (self-assembling monolayers) as corrosion inhibitors

Many applications require the assembly of nanoparticles in thin film form and the ability to tailor the interaction between the particles [Mayya et al., 2003]. Therefore, much interest has been focused on the cluster, especially the films of nanoparticles. An effective approach is the Langmuir–Blodgett (LB) technique [Chen, 2001]. A monolayer or multilayer of nanoparticles can be formed on the surface of substrate. Sastry and co-workers [Mayya et al., 2003] obtained fatty amine–gold nanoparticle monolayers, which could be transferred by the LB technique on different substrates. Many authors have study the property of the nanoparticles LB films, for example, using the electrochemical methods, Chen [2001] investigated the interfacial dynamics of nanoparticle Langmuir–Blodgett thin film. Another effective approach is the self-assembled monolayer. Self-assembly of nanoparticles into two-dimensional (2D) and three-dimensional (3D) super lattice structures [Zhao et al., 2002, Cheng et al., 2002] which are thought to be indispensable components in Nano scale chemical and biological sensor devices. In this field, some groups investigate the preparation methods of

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nanoparticle SAMs. Other research groups concentrate on the properties of nanoparticle SAMs including the physical, chemical, and biologic properties [Pileni, 2001, Murray et al., 2000].

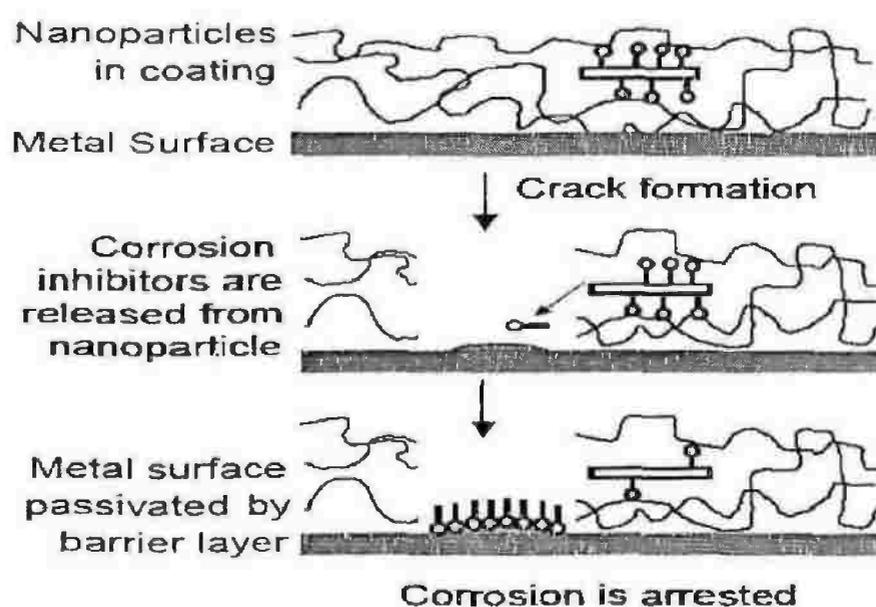
Besides the transmission electron microscopy (TEM), atomic force microscopy (AFM) and X-ray diffraction (XRD) [Stoeva et al., 2003], Electrochemistry is also an effective method to characterize the nanoparticle SAMs and other SAMs such as alkyl sulfhydryl SAMs. Cyclic voltammetry (CV), polarization curve, and electrochemical impedance spectroscopy (EIS) are the primary methods to investigate the electrochemical properties of SAMs and nanoparticle SAMs especially on the surface of metal electrode. For example, utilized CV method to study the interfacial electron-transfer processes of Au nanoparticles modified electrode. Although lots of studies have focused on the properties of the nanoparticle SAMs modified electrode, to the best of our knowledge,

The nanoparticles can form a self-assembled film on the surface of copper. Utilizing electrochemical methods of CV and EIS, Au and Ag nanoparticles modified copper electrodes are studied. The results indicate that the SAMs may be a mixed monolayer in which the nanoparticles and sodium oleate molecule are included, and has a effective corrosion inhibition for copper in corrosive solutions. TEM was used to observe the Au and Ag nanoparticles; XPS was utilized to investigate the component [Li et al., 2006].

Use of corrosion prevention coatings is the most effective measure for slowing or preventing corrosion. These coatings provide a barrier to the (harsh) external environment. In addition, if the coating is damaged it should also provide active corrosion protection – i.e. corrosion inhibition, even to the now uncoated area. A patented active corrosion inhibitor has

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been developed that can provide smart corrosion protection. A method to surface modify nanoparticles with releasable corrosion inhibitors was developed. The corrosion inhibitors are anchored to the surface of the nanoparticles and are released from the nanoparticle surface through a trigger provided by the corrosion process itself. Thus, the inhibitors remain in the coating until needed and when corrosion occurs they release, migrate to the metal surface and arrest corrosion (Figure 2).



**Figure (2)** Corrosion arrested by release of corrosion inhibitor

This smart mechanism uses the corrosion inhibitor only when needed and allows long-term corrosion protection. Current inhibitors are selected to be slightly soluble in water, and slowly but continually leach out of the coating. In contrast, the new corrosion inhibitor additives are released only when needed to arrest corrosion. This smart, release-on-demand mechanism extends the life of coating, since the inhibitors are not continually being lost [Elliott and Cook, 2007].