CHAPTER (1)

1. INTRODUCTION

1.1 General Background on Micelles

Surfactants (surface active agents) are molecules that possess hydrophilic and hydrophobic character. They may aggregate under favorable conditions in water and form microscopic domains called micelles [1]. The original description of these aggregates dates back to Hartley [2].

Numerous studies have been performed in attempts to understand this interest field, for example, in the period from 1980 to 1990, 350 reviews (not primary articles) have been published on this subject [3-5]. The most studies in liquid/liquid electrochemistry are the works on micelles in physical chemistry, analytical chemistry [7,8] and in electrochemistry, but electrochemistry remains an important tool for studing micelles.

At low concentrations in water, the surfactant molecules are simply dissolved. On increasing surfactant concentration, the solution conductivity increases and the surface tension decreases upon reaching a certain concentration at which the surfactant molecules start to aggregate with the nonpolar tails of the molecule being packed together in the interior and the hydrophilic heads pointing outwords, forming roughly spherical objects called micelles [9]. The concentration at which this aggregation occurs is known as the critical micelle concentration (CMC). Above the CMC the concentration of unassociated surfactant remains virtually constant. Further addition of monomer causes an increase in the number of micelles. Thus, the surface tension and conductance remain unchanged above the CMC [9].

There is a relatively small range of concentrations separating the limit below which virtually no micelles are detected and the limit above which virtually all additional surfactant forms micelles. Many properties [10,11] of surfactant solutions, if plotted against the concentration, appear to change at different rate above and below this range. By extrapolating the logarithm of such a property above and below this range until they intersect, a value may be obtained known as the critical micelle concentration (CMC).

The size of the micelles depends on the nature of the surfactant and the solvent, the typical size for most micelles is between 60 and 100 monomers, of typical size 3 to 6 nm [12].

Most often, micelles are formed within aqueous solutions. In these so-called normal micelles, the hydrophilic moiety of the surfactant points outword. In a nonpolar medium surfactant can aggregate to from reverse or inverse micelles [1,13], Fig. (1).

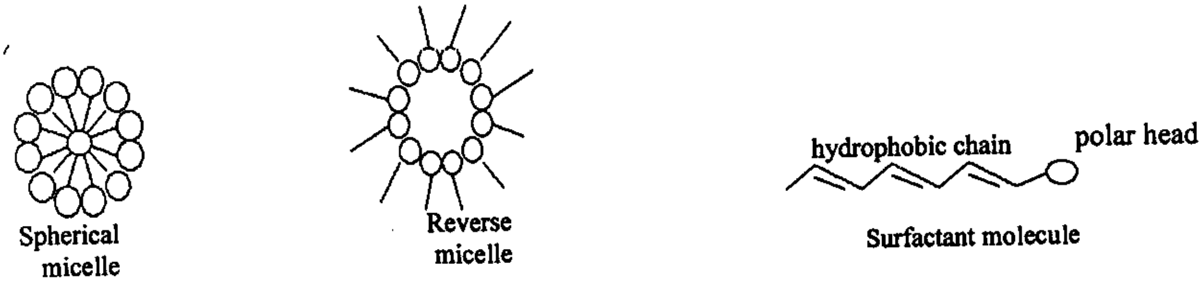

Fig.(1): Schematic representation of organized structures of surfactants in different media.

A number of experimental techniques including light scattering, NMR spectroscopy and fluorescence probe measurements have been used to characterize micelles in aqueous solutions [14]. The applications of micelles in various areas are numerous [15-18]. Micelles exhibit some features of biological membranes by providing a charged interface and polar head [19]. They are known for their ability to permit normally water-insoluble compounds to solubilize in aqueous solutions. When a hydrophobic molecule is solubilized, it is mainly located inside the micelles [20]. The distribution of the guest molecules between aqueous and organic domains in micelles is of importance in many industries [21,22].

1.2 Electrochemistry in Micelles and Microemulsion

Electrochemistry is an important tool for studying micellar and microemulsion systems with greater simplicity and the same versatility as NMR. Any electrochemical technique that allows the determination of the diffusion coefficient of an electroactive substance, can be used for measuring diffusion in micelles and microemulsion systems. The information obtained depends on the nature of the electroactive probe, its relative compartmentalization (partitioning) between the continuous and discontinuous pseudophases, and interactions with the interfacial surfactant. The choice of the electroactive probe is the key for obtaining meaningful data. According to Chokshi, Qutubuddin, and Hussam [23], who have recently discussed this problem, the electroactive probe must minimize the disruption in the nature of the microemulsion aggregate, undergo diffusion-controlled charge transfer at the electrode surface, be nonpolar in oil-in-water systems, and not be significantly adsorbed onto the electrode surface. Of course, the probe must be electrochemically reactive within the potential range governed by the electrode material and the microemulsion medium. Ferrocene meets these requirements in many microemulsions.

Electrochemical techniques that have been used for such studies include polarography [24-26], cyclic voltammetry [27-32], rotating disk voltammetry [32-38], chronoamperometry/chronocoulometry [28,39], and chronopotentiometry. The advantages of these electrochemical techniques are as follows:

1- These techniques are inexpensive compared to other techniques.
2- Fast and relatively easy characterization are possible.
3- No physical properties required, except viscosity which is required to calculate the droplet size in any technique.
4- The ectrochemical techniques provides self diffusion coefficient while other methods give self diffusion and/or collective diffusion.
5- Opaque systems can be characterized.

Also, electrochemical techniques can be used to study redox and related chemical reactivity in the microheterogeneous environment of microemulsion [40,41].

1.3 Literature Survey on Electrochemistry in Micelles

1.3.1 Determination of CMC of surfactant

An electrochemical method has been developed in which polymer membrane ion-selective electrodes have been used to determine the CMC of charged surfactants [42]. Because the electrodes are sensitive to the concentration of ions in solution, increasing the surfactant concentration in solution changes the potential reading. Above the CMC, however, the concentration of monomeric ions in solution changes only slightly and accordingly, the electrode potential varies very little. The CMC is the concentration at which the line through the region below the CMC and a line through a plateau above the CMC intersect. For neutral surfactants, it is possible to determine the CMC through a similar but more indirect technique using hydrophobic "probe" molecule which can partition between the micellar and aqueous phases, held at constant concentration, and a CWE selective for an ion in the probe [43].

Ferrara, Wei-Hua and Freiser [43] determined the CMC of three neutral surfactants, Triton X-100, Triton X-162 and Triton X-305 using wire electrodes coated with tetraheptylammonium chloride (THAC) or benzalkonium chloried (BAC) and a constant concentration of the appropriate chloride. The values determined with the THAC electrodes and $10^{-4.4}$ M THAC solutions are in agreement with previously reported values. When 10^{-5} M THAC or 10^{-4} or 10^{-5} M BAC was used, the measured CMC values were lower than expected.

Takeoka et al. [44] applied electrochemical technique (cyclic voltammetry) for studying nonionic surfactant, α-(ferrocenylundecyl)-ω-hydroxy-oligo(ethylene oxide) (FPEG), and showed that, the cyclic voltammograms (ν = 10 mV/s) of the FPEG solutions change with the concentration; below the critical micelle concentration (CMC), the voltammetric shape is of a typical surface-confined species, while above the CMC the diffusion-controlled waves are superimposed at the cathodic side of the surface waves, and far above the CMC the voltammetric shape is of a typical diffusion-controlled species.

Berlot et al. [45] studied the self-aggregation properties of a pyrrole-substituted cationic surfactant using different techniques, including conductivity and surface tension measurements, potentiometry with a surfactant-selective electrode and cyclic voltammetry. Potentiometry gave good results for the determination of its critical micelle concentration (CMC) as well in pure water as in electrolytic media. Furthermore, inspite of the highly irreversible oxidation of the pyrrole group contained in the surfactant, cyclic voltammetry afforded a fast and valuble estimation of the CMC from peak current and peak potential variations.

1.3.2 Diffusion in Micelles

There are numerous electrochemical attempts to study micelles [46,47]. These studies include the micelles of electroinactive [48,49] and electroactive [46-49] surfactants. Kuwana et al. [50] have estimated the diffusion coefficient of the micelles of an electroinactive surfactant, Tween 20, by using a probe molecule, ferrocene, which is solubilized in the micelles.

Dayalan et al. [51] reviewed the measured diffusion coefficients of ferrocene in micellar systems of CTAB, SDS and DTINS electrochemically. They studied the effects of probe partitioning equilibria, kinetics and pseudophase structure on the apparent diffusion coefficients.

Avranas and Sazou [52] reported the apparent diffusion coefficients of 2,2'-dinitrobiphenyl in SDS, CTAB and Tween 80 micelles. The electrochemical data showed that the order: $(D_{app})_{Tween} < (D_{app})_{CTAB} < (D_{app})_{SDS} < D_W$ is valid. They used the apparent diffusion coefficient to estimate the fraction of the electroactive substance that bounds to micelles.

Liu et al. [53] have been reported the micelle diffusion coefficient of SDS with different micelles shape in aqueous and water-ethanol solutions, which determined by cyclic voltammetry without any probe. It was found that the diffusion coefficient decreases with an increasing SDS concentration.

Mandal [54] used polarographic technique to estimate diffusion coefficients of the micelles containing an electroactive probe molecule and thus a measure of micelle size and interactions. Also, he reported a study to determine the actual self-diffusion coefficients of the micelles using cyclic voltammetric technique with suitable electroactive probe.

1.3.3 Solubilization of Electroactive Molecules in Micellar Solution

The applications of micelles in various areas are numerous [15-17,55]. They are known for their ability to permit normally water-insoluble compounds to solubilize in aqueous solutions. The solubilization of a hydrophobic molecule in micellar solution is of importance in many industries [19,20]. The use of micellar solutions as a mean of solubilization of electroactive molecules was recognized very early by Hayano, Shinozuka, and co-workers [56-58]. This solubilization has given rise to a new extensive array of studies concerning electrochemistry in organized assemblies, such as the early work of McIntire et al [59]. This field has been developed by Rusling and co-workers [60,61], Genies and Thomalla [62].

It is not possible to give particular value for the partition constant of a given substance in a micelle. This depends on the location of the substance inside the micelle, since the effective concentration of the substance varies accordingly [63].

Georges and Desmetter [35] measured the solubilities of ferrocene in aqueous 0.1 NaCl solution of SDS, CTAB, Brij 35 by using spectrophotometry and by limiting current measurements in direct current voltammetry.

Fisicaro et al. [64] made a voltammetric study of a series of differently substituted benzenediols, carried out in aqueous anionic micellar solutions. The partitioning of the probes between the bulk aqueous and the micellar pseudophase affects both the obeserved currents and the half-wave potentials. The results are discussed in terms of probe-aggregate interactions and compared with kinetics of electron transfer reactions involving benzenediol/quinone couples.

1.4 General Background on Microemulsions

The term microemulsion was first coined by Schulman and Hoar [65]. Microemulsions are thermodynamically stable isotropic dispersions consisting of microdomains of oil and/or water stabilized by an interfacial film of surface active molecules [66]. Often it is also contain a cosurfactant usually a short chain alcohol, which is critical in reducing the interfacial tension between the droplets and the continuous phase to near zero, and an electrolyte such as NaCl, may also be included in the mixture.

Microemulsions have an extremely small sizes in the range of 50-500 A^0 versus a typical diameter of one micron (10,000 A^0) for coarse emulsions [67].

The phase behavior and microstructure of microemulsion depend on surfactant type and concentration, cosurfactant type and concentration, electrolyte type and concentration, temperature and pH. These parameters are observed in numerous thermodynamic studies [68,69].

Microemulsions are classified and organized into specific structures [70]. In mixtures with high water content, i.e, oil-in-water (O/W) microemulsions, oil is confined to discrete droplets and water acts as a continuous phase. The oil droplets are surrounded by surfactant and cosurfactant [71] or by interface, which diffuse in a continuous phase of water and referred to as a lower-phase microemulsion. Similarly, water-in-oil (W/O) microemulsions, have high oil content and water droplets surrounded by interface which diffuse in a continuous phase of oil and referred to as upper-phase microemulsions. If both the oil and water content of the solution are significant, the so-called bicontinuous micremulsions are formed. In such systems, both oil and water act as continuous phases [72].

Microemulsions also may be classified according to their surfactant charge. Surfactants can be ionic (either anionic or cationic), zwitterionic and nonionic.

Since microemulsions are microscopically heterogeneous, it can be solubilize both oil-soluble and water-soluble compounds due to presence of aqueous and non-aqueous domains.

The literature survey on microemulsions is quite encompassing and has recently reviewed by Holt [73] and Friberg [69]. Microemulsion have been extensively studied using x-ray and light scattering [74-78], ultracentirfugation [79], spin label probes, dielectric relaxation fluorescence probes [80,81], neutron scattering [82-84], and NMR [85,86].

Model microemulsion systems have been developed by several authors [85,87-89]. Chou and Shah [90] investigated the effect of various electrolytes on solubilization in an oil continuous microemulsion containing a petroleum sulfonate as surfactant and found solubilization to be maximal at certain electrolyte concentrations.

Qutubuddin [87] has developed both pH-independent and pH-dependent systems [87,88]. pH-independent systems contain an alkyl arylsulfonate as the surfactant while the pH-dependent systems [89] contain oleic acid as the surfactant. The size and charge of microemulsion droplets have been measured by Qutubuddine et al. [74] using electrophoretic laser light scattering. He has also investigated the effect of additives [91] like polymers on the phase behavior of microemulsion.

Winsor's [92] assumed that microemulsion structure depends on the natural curvature of the surfactant layer formed at the water /oil interface. This natural curvature is closely related to the ratio of the surfactant lipophile–oil interaction energy, E_{lo}, to the surfactant hydrophile-water interaction energy, E_{hw}. When $(E_{lo}/E_{hw}) << 1$, the natural curvature of the surfactant layers favors formation of small oil droplets in water, while if the ratio $(E_{lo}/E_{hw}) >> 1$, an upper phase microemulsion coexists with an excess aqueous phase. As (E_{lo}/E_{hw}) approaches unity the natural curvature of the surfactant layers tends to decrease and bicontinuous structures may exist.

Schulman et al. [93] postulated that the transient interfacial tension has to be negative for the spontaneous uptake of water or oil in microemulsions. During the process of microemulsion formation one phase breaks up into the maximum number of droplets. The diameter of these droplets depends upon the interfacial area produced by the surfactant molecules. The transient interfacial, e.g the spontaneous tendency of the interface to expand produced by the mixing of the components became zero or a very small positive value at equilibrium.

Gerbacia and Rosano [94] have determined that the diffusion of surfactant molecules across the interface is the main factor for reducing the interfacial tension temporarily to zero as well as for the formation of microemulsions. It has also been shown from thermodynamic consideration that if the interfacial tension is very low, in the order of 10^{-4} to 10^{-5} dynes/cm, stable and spontaneous formation of microemulsions take place.

Microemulsions have their importance in application in enhanced oil recovery [95,96], pharmaceutics, cosmetics, extractions, photochemical and polymerization reactions. Other areas in which the application of microemulsions are emerging include precious metal recovery, coatings technology, advanced fuel technology and targetted drug delivery [97,98].

1.5 Literature Survey on Electrochemistry in Microemulsion

1.5.1 Diffusion in conductive microemulsions .

Electrochemical measurements on microemulsion systems are rare since this technique is recently applied to microemulsion systems.

Mackay et al. [99] suggested that electrochemical techniques can be used to obtain information about the microstructure of microemulsion. They also used dc-polarography to measure diffusion coefficients, which were in agreement with those determined from quasi-elastic light scattering (QELS) and were used as evidence for the microdroplet structure [100]. They also reported that the diffusion coefficient value (D^o) of oil soluble probe (1-dodecyl-4-cyanopyridinum ion) is independent of the amount of water from 35-65% (bicontinuous microemulsion) in sodium cetylsulfate (SCS)/water/pentanol/octane system, and used the same probe in octane/cetyltrimethyammonium bromide (CTAB)/1-butanol /water microemulsions for diffusion measurements at high water content. Values of D^o obtained from dc-polarography were in agreement with those determined from quasi–elastic light scattering, but for SCS and CTAB microemulsions with water content, agreement of polarographic D^o- values with QELS was not as good. Because of polydispersity, polarography provides apparent self-diffusion coefficient, while QELS can give a self-diffusion coefficient, a collective diffusion coefficient, or a combination of both.

Chokshi et al. [32] applied two electrochemical techniques, cyclic voltammetry and rotating disk voltammetry to characterize oil-in-water microemulsions. Diffusion coefficients of n-octane/cetyltrimelthylammonium bromide/n-butanol/water microemulsions were determined using ferrocene as the hydrophobic electroactive probe and NaBr as the electrolyte. The diffusion coefficients were compared with values obtained from QELS. The differences observed between electrochemical and light scattering measurements are due to the different modes of diffusion probed by these techniques.

Dayalan et al. [51] measured diffusion coefficients in oil–in-water microemulsions of CTAB, SDS and DTINS electrochemically. The effects of probe partitioning equilibria, kinetics and effects of pseudophase structure on the measurement of apparent diffusion coefficients were critically discussed.

Mayers et al. [101] reported diffusion coefficients of some electroactive probes in the oil-in-water sodium dodecylsulfate 1-pentanol/ dodecane/0.1M $NaCl_{(aq)}$ microemulsion using cyclic voltammetry. Changes in diffusion coefficient of the probes indicate droplet microstructure of the microemulsion at high water content and a bicontinuous structure at lower water content.

Santhanalakshmi and Vijayalakshmi [102] studied the electrochemical properties of cobalticenium hexafluorophoshate in water and in oil-in-water (O/W), dodecane-SDS-n-pentanol-water microemulsions through cyclic voltammetry. Microstructural and dynamic properties of microemulsions, such as droplet diffusion coefficients, surfactant aggregation number, fraction of the free ions, and number density of droplets were evaluated from electrochemical data.

1.5.2 Diffusion Studies with Microelectrodes

In the microemulsion of type W/O, the continuous phase is of neat oil and is quite resistive. It is impossible to obtain measurements of this system with conventional sized electrodes, since the iR drop of this type of microemulsion is of large magnitude. Microelectrodes with dimensions in the μm range are nearly unaffected by iR drop, and can be used to study diffusion in highly resistive system.

Chen and Georges [103] used steady-state microelectrodes voltammetry to study diffusion in W/O microemulsion systems. They used ferrocene as oil-soluble probe, in SDS/dodecane/1-pentanol/water systems. The diffusion coefficient of ferrocene reflected the micro-viscosity of the oil phase, rather than the bulk viscosity of the microemulsion.

1.5.3 Partitioning and equilibria in Microemulsions

The distribution of solute between aqueous and organic domains in micelles and microemulsions is important in many industries [18,104-107]. The dispersed phase in micellar and microemulsion systems can not be isolated from the continuous phase without drastically affecting the morphology. So, the measurement of the distributsion coefficient (P) for partitioning into the dispersed phase in these systems can not be made by normal analytical methods applicable to macroscpic two-phase system. The distribution in micellar and microemulsion systems is different from macroscopic two-phase systems due to modifying effects of the interface.

Qutubuddin et al. [38] determined the distribution coefficients of different probes, ferrocyanide ion and substituted para-phenylene-diamines (4-amino-3-methyl-N-ethyl-N-(β-sulfoethyl) aniline (PPDI) and 4-amino-3-methyl-N,N-diethylaniline (PPD2) in oil-in-water microemulsions of cetyltrimethylammonium bromide (CTAB) and octadecyldimethyl betaine (C_{18}DMB). The measured diffusion data converted to distribution coefficients (P). These distribution coefficients (P) values were shown to be a lower bound on the actual distribution coefficients because of neglecting probe-droplet kinetics near the electrode. The order of binding was ferrocyanide << PPD1 << PPD2 in CTAB microemulsion, with the same binding order of PPD1 and PPD2 in C_{18}DMB microemulsion.

Mayers et al. [101] studies the effect of probe partitioning on the electrochemical formal potentials in microheterogeneous solutions using cyclic voltammetry and chronocoulometric techniques. Ferrocene, methyl viologen and ferricyanide ion used as probes to demonstarte the limiting cases of the relationship between these parameters in the microheterogeneous systems of sodium dodecyl sulphate (SDS)/1-pentanol/dodecane/0.1 M NaCl aqueous microemulsions. The shift in formal potential with microemulsion composition were related to changes in both partitioning constants and diffusion coefficients.

Mackay [108] measured the diffusion coefficients of ferricyanide and cadmium ions in ionic microemulsion of cetyltrimethylammonium bromide using dc-polarography. The results showed that electrostatically bound aqueous ions have the same value of D as do surfactant-like ions such as long alkyl-chain pyridinium ions.

Santhanalakshmi and Vijayalakshmi [102] studied the electrochemical properties of cobalticenium hexafluorophosphate in water and in oil-water (O/W), dodecane/SDS/n-pentanol/water microemulsions, using cyclic voltammetry, conductivity, and viscosity measurement at 300° k, and reported that the cobalticenium ion when added to microemulsions exhibits the partitioning and diffusion phenomena similar to ferrocene or any other electroactive probes that are strongly dependent on microemulsion compositions.

1.5.4 Electrochemical reactions in micelles and microemulsions

The electrochemical reduction of 2,2'-dinitrobiphenyl in anionic micellar solutions [109] is investigated by polarography and cyclic voltammetry. The reduction took place in two irreversible electron transfer steps. The half-wave potentials and the currents for both reduction steps depended on the type of micelles.

The electrochemical reduction of methyl viologen was investigated in cationic, anionic and non-ionic microemlsions [44]. Cationic CTAB, anionic SDS and non-ionic Triton X-100 model surfactants were used. The reduction process took place in two reversible single-electron transfer steps. The half-wave potentials for both reduction steps and the diffusion currents depended mainly on the type and composition of microemulsion. The measured D^{o}-values for MV^{+2} indicated its binding to the oil droplets in SDS system but no binding in cationic and non-ionic microemulsion .

Garcia et al. [110] reported a coulometric initiation of acrylamide polymerization in Aerosol OT/toluene/water (water-in-oil) inverse microemulsions, using Pt/Nafion solid polymer electrode (SPE). They reported that acrylamide (cosurfactant) induced electron transfer in highly resistive microemulsions of the quaternary water-acrylamide/bis (2-ethylhexyl) sulfosuccinate (AOT)/toluene systems. Threshold cosurfactant (acrylamide) levels exist, below which electron transfer to or from Pt ultramicro-electrodes is retarded and above which electron transfer is greatly facilitated. This threshold phenomenon attributed to interfacial surfactant packing.

Generally, surfactants have been widely used as brighteners in the electroplating industry [111] and have promising roles in advanced battery design [112]. Surfactants such as gelatin and Triton X-100 began to be used routinely in electroanalytical chemistry to suppress streaming maxima at the dropping mercury electrode (DME). Surfactants adsorb at the mercury-solution interface and retard streaming of solution near the DME, supressing unwanted covection currents [113-115]. Adsorption of surfactants on the electrode can have large effects on the kinetics of heterogeneous electron transfer reactions at the DME.

Many investigations have demonstrated that coulombic and hydrophobic interactions with surfactants can stabilize various electrochemically produced ion radicals [3]. Electrochemical methods have been used for controlling electrochemical reactions with surfactants as well as aggregate characterizations [1,17]. Novel work was being done with surfactant microsturctures to control chemical and photochemical reactions.

1.6 Background on Electrochemical Techniques

1.6.1 Cyclic voltammetry (CV)

General reviews on cyclic voltammetry have been presented by several authors [116,117]. Cyclic voltammetry is often the first experiment performed in an electrochemical study of a chemical compound, a biological material, or an electrode surface. The main advantage of cyclic voltammetry is that, its capability for rapid observing the redox behavior over a wide potential range. The voltage applied to the working electrode is scanned linearly from an initial value E(i) to a predetermined limit E(f) (known as switching potential) where the direction of scan is reversed. The controlling potential which is applied across the working and reference electrodes considered as an excitation signal. The excitation signal for cyclic voltammetry is a linear potential scan with a triangular wave-form. This triangular potential excitation signal sweeps the potential of the electrode between two values, an initial value E(i) to a predetermined limit E(f). At point E(f) the first cycle is completed and the scan direction is reversed.The current is measured throughout the experiment and the resulting I-E curve is called a voltammogram. The characteristic peaks in the voltammograms are caused by the formation of a depletion layer in solution near the electrode surface. The position of peaks on the potential axis is related to the formal potential of the redox process.

Cyclic voltammetry has found to be practically useful in investigations of mechanisms of oxidation and reduction of a number of organic substances [118-122]. From the magnitude of anodic peak current $I_{p,a}$ or cathodic peak current $I_{p,c}$ and from the potentials at which the peak current are observed $E_{p,a}$ and $E_{p,c}$ information on reversibility or irreversibility of the system and on chemical reaction accompanying electrode processes can be obtained.

The behaviour of the current during the potential scan is given by the following equation [123]:

$$i = nFAD(\partial C/\partial X)_{x=0} \qquad (I.1)$$

where,

i is the current, amps,

n is electron stoichiometry total,

A is the electrode surface area , cm^2,

F is the Faraday constant , coulomb per equivalent

Nicholson and Shain [124] have derived numerically, the expression of the peak current of the linear sweep voltammetric wave in case of planar diffusion. This expression may be written as follows:

$$i_p = 0.446nFAC_A\,(nF/RT)^{1/2}\ \nu^{1/2}\ D^{1/2} \qquad (I.2)$$

where,

i_p is the peak current, amps,

ν is the sweep rate, Volt /sec,

At 25^0 C equation (I.2) can be given as:

$$i_p = (2.69x10^5)\ n^{3/2}\ D_o^{1/2}\ A\ \nu^{1/2}\ C_o \qquad (I.3)$$

This expression is called Randlles and Sevcik [118] equation.

For the reversible reactions, the peak potential seperation is given by [117,123]

$$\Delta E_p = E_{p,a} - E_{p,c} = 59/n \ \ mV\ at\ 25\ ^oC \qquad (I.4)$$

where $E_{p,a}$ and $E_{p,c}$ are the anodic and cathodic peak potentials, respectively.

The position of the peak potential E_p is independent of sweep rate, while the peak current is proportional to $\nu^{1/2}$. The ratio of anodic peak current $i_{p,a}$ to cathodic peak current $i_{p,c}$ [116,117,125,126] is given by:

$$i_{p,a}/i_{p,a} = 1 \qquad (I.5)$$

For a reversible electrode process Nernst eqution [117] is given as follows:

$$E_{1/2} = E^{o} + RT/nF\ln(D_o/D_R)^{1/2} \qquad (I.6)$$

and the half-wave potential $E_{1/2}$ described as:

$$E_{1/2} = (E_{p,a} + E_{p,c})/2 \qquad (I.7)$$

For irreversibility where the rate of electron transfer is sufficiently slow with respect to potential sweep rate, as the sweep rate is increased the rate of mass transport increases and the potential of response in (CV) is shifted very cathodically for reduction and very anodically for oxidation processes with respect to the standard potential. Generally, for a totally irrerversible reactions there is no peaks observed on the reverse scan. The peak current for irreversible process [124] at 25° C is given as follows:

$$i_p = (3.01x10^5)n(\alpha n_a)^{1/2}C_AD_A{}^{1/2}\nu^{1/2} \qquad (I.8)$$

where,

α is the transfer coefficient,

n_a is the number of electrons transferred through the rate-determining step.

The peak potential E_p for irreversible reaction depends on sweep rate and is given by the following equation [124]:

$$E_p=E_e^o-RT/\alpha\, n_aF[0.78-\ln(n_aFD/K^{o2}RT)^{1/2}]-(RT/2\alpha\, n_aF)\ln(\nu) \qquad (I.9)$$

where,

E_e^o is the standard electrode potential,

K^o is the standard rate constant.

The separation of E_p and $E_{p/2}$ is given as follows:

$$[E_p - E_{p/2}] = 48/\alpha n_a \quad \text{mV, at } 25^\circ\text{C} \qquad (I.10)$$

The kinetic parameters, k^o and αn_a of the electrode reaction were calculated using the following equation [127]:

$$E_p= - 1.14\, (RT/\alpha\, n_aF)+(RT/\alpha n_aF)\ln(k^o_{f,h}/D^{1/2})-RT/2\alpha n_aF\, \ln(\alpha n_a\nu) \quad (I.11)$$

1.7 Rotating Disk Voltammetry (RDV)

Rotating disk, rotating ring, streaming mercury and vibrating electrodes are examples of electrochemicals techniques in which the electrode moves with respect to the solution. These systems are called hydrodynamic methods in which the electrode is a motion or involving connective mass transport of reactants and products.

The most practical form of an electrode for which a completely rigorous hydrodynamic treatment can be given is the rotating disk electrode (RDE) [128-132]. A completely rigorous hydrodynamic treatment has been given by Lavish 1942 [128].

The advantages of hydrodynamic method is that a steady state is attained quickly so measurements can be made with high precision and double-layer charging does not enter the measurement. Also, the rates of mass transfer at the electrode surface are much larger than the rate of diffusion, so the relative contribution of the effect of mass transfer to electron transfer kinetics is smaller. Levich [133] solved the mass-transfer equations of the RDE. The limiting current for a reaction controlled only by mass transfer is given by the relation:

$$i_L = 0.62\, nFA(D^{2/3})(v^{-1/6})(\omega^{1/2})C \qquad (I.12)$$

where,

i_L is the limiting current , amps ,

F is the Faraday's constant, 96487 coulomb/equivalent,

A is the electrode surface area, cm^2/sec,

ω is the angular velocity, rad/sec = $2\pi N/60$,

(where N is the number of rotations per min),

v is the kinematic viscosity, gm/cm.sec,

C is the bulk concentration of electroactive species, $mole/cm^3$.

An important modification of equation (I.12) was proposed by Gengory and Riddiford [134], and after a careful check of the accuracy of limiting currents over a wide range of rotation rates and as a function of temperature. This modification involved replacing the constant 0.62 by the quantity:

$$\frac{0.554\,(Sc)^{-2/3}}{0.8934 + 0.316\,(Sc)^{-0.36}} \qquad (I.13)$$

where Sc is called a Schmidt number and is equal to v/D. This correction is applied within 1% for Schmidt number (Sc > 250). But for the investigated systems, the correction term (Sc) is negligible, so that the Levich equation (I.12) is valid. Thus, the diffusion coefficients were simply obtainned from the slope of the limiting current, (i_L), versus square root of angular velocity (ω) plot. The diffusion coefficient was measured by Landau [135] in $CuSO_4$-H_2SO_4-Glycerol system. The theory of the rotating disk voltammetry technique is reviewed by several authors [136-140] and the current distribution at RDE is discussed by Newman [139].

The current at a given potential at the RDE; assuming the simple reaction ($A + ne^- = B$); can be given as:

$$i = i_L \{C - C_{(x=0)}\}/C \qquad (I.14)$$

The potential E on the rising portion of the voltammogram is related to the half-wave potential and the limiting current Nernstain voltammetric wave equation [117]:

$$E = E_{1/2} - RT/nF \ln [(i_L - i)/i] \qquad (I.15)$$

where,

i is the current at potential E.

and

$$E_{1/2} = E^{\circ} + RT/nF \ln (D_R/D_o)^{2/3} \qquad (I.16)$$

It is apparent from equation (I.15) that the half-wave potential and the number of electrons transferred can be obtained from a plot of E versus ln $[(i_L - i)/i]$.

The equations for the RDE will not apply at very small or very large values of ω. The lower limit of ω is governed by the condition that the disk radius $R_1 >> 3 (\nu/\omega)^{1/2}$, that is, $\omega > 10 \nu / R_1^{2}$. The upper limit for ω is governed by the onset of turbulent flow, this occurs at the RDE at a

Reynolds number, Re (critical), is a bout $2x10^5$ [141,142]. Where Re (critical) is defined as:

$$Re\ (critical) = \omega\ (R_1)^2 / v$$

The condition for non-turbulent flow is that $\omega < 2x10^5\ v / R_1^2$.

It was found practically that, the maximum rotation rates are set at 10,000 RPM or 1000 sec^{-1}. Therefore, the most available rotation rate lies within the ω values in between:

$10\ sec^{-1} < \omega < 1000\ sec^{-1}$ or $100\ RPM < \omega < 10,000\ RPM$.

1.8 Chronocoulometry (CC)

Chronocoulometry is one of the classical electrochemical techniques that used in electroanalytical chemistry. The integration of current–time response (chronoamperometry) produces the charge passed as a function of time and this process is called chronocoulometry. Chronocoulometry is an extremely valuable technique for the direct measurement of adsorption of electroactive species [143-148]. This technique was first popularized by Anson [144] and co-workers. Chronocoulometry is easily applied to fast reactions, and the measured signal are least distorted by non-ideal pontential rise. Also, chronocoulometry offers better signal-to-noise ratios. The contributions to the measured charge (Q_d) from double layer charging and from electrode reactions of adsorbed species can be distinguished from those due to diffusing electroreactants. Chronocoulometry is valuable for the study of surface processes at the electrode surface [143-148].

A typical current potential curve (recorded under steady-state conditions) for the reduction of electroactive species at the electrode surface, no current flows until the potential reaches values near the reduction potential of the reactant, at which a sharp rise of current is obtained. As the potential is made still more negative, the current eventually levels off at a limiting value where every reactant molecule reaches the electrode is immediately reduced. If the experimental conditions are arranged so that the reactant is transported to he electrode surface by means of a linear diffusion (i.e. unstirred solution, flat electrode), an equation originally derived by Cottrell [143] can be used to calculate the current that flows at any time after the application of the potential step from initial value E(1) to sufficiently negative value E(2) to enforce a diffusion–limited current, the equation is given as follows:

$$i = nFAC(D/\pi t)^{1/2} \qquad (I.\ 17)$$

where t is the time following the potential step. This current is actually composed of two components; Cottrel current and the charging current i(c) that flows to charge up the capacitance at the electrode/electrolyte interface[147].

The total charge in the presence of adsorption of the reactant for the forward step is given by the relation:

$$Q_{tot} = (2nFAC_oD_o^{1/2}\ t^{1/2})/\pi^{1/2} + Q_C + Q_{ads} \qquad (I.18)$$

where,

Q_c is the charge flowing into the interfacial capacitance,

Q_{ads} is an extra charge provided by the adsorbed reactant and t is time.

By using Faraday's law the amount of Q_{ads} is given as following:

$$Q_{ads} = nFA\Gamma_o \qquad (I.19)$$

where Γ_o is the amount of the adsorbed reactant in moles/cm^2.

The plot of Q_{tot} versus $t^{1/2}$ (called the Anson plots) will have intercept equal to the amount ($Q_c + nFA\Gamma_o$). To obtain the amount of the adsorbed reactant Γ_o it is important to know or to calculate the interfacial capacitance charge. This presents no problem when the adsorption of a reactant produces little or no change in the interfacial capacitance. The value of Q_c can be measured in a background solution containing no reactant species. By subtracting the intercepts of equation (I.18) in absence and in presence of reactant species an approximate value of $nFA\Gamma_o$ can be obtained.

However, adsorption of a reactant frequently produces a significant charge in the interfacial capacitance. The capacitance charge Q_c will be somewhat different in background experiment from that in the presence of significant adsorption. This difficulty can sometimes be overcome by double-potential step chronocoulometry in which the electrode potential is returned to its original value E(1) [144]. The response of the reverse step is related by following equation [144,145,149]:

$$Q_r = Q_c + (2nFAD_o^{1/2}C_o[\theta])/\pi^{1/2} + nFA\Gamma_R \qquad (I.20)$$

where,

t is the total time (sec),

$\theta = \zeta^{1/2} + (t - \zeta)^{1/2}$

ζ= forward step width, sec

Γ_R is the amount of adsorbed product (moles/cm^2)

In the absence of product adsorbed, the difference of intercepts of Q_{tot} versus $t^{1/2}$ and Q_r versus θ plots gives the direct measurements of adsorbed species [144-147] which is in general:

$$\text{Intercept (1)} - \text{Intercept (2)} = nFA\,(\Gamma_o - \Gamma_R) \qquad (I.21)$$

In addition to study the adsorbed species, chronocoulometry can be used to study the homogeneous chemistry of oxidant and reductant [117,148].