CHAPTER

CHAPTER (I)

INTRODUCTION

Compounds possessing quinoid structure play an important role in electron and proton transfer reactions in biological systems [1-3]. For instance, the biological activity of vitamin K, which is a 1,4-naphthoquinone, is due to its role as an oxidising agent [4]. Vitamin K group are present in vegetables where they seems to play an active role in photosynthetic mechanisms [5]. They also play a role in cellular respiration as electron transporters [6]. In the human body, they are synthesized by microorganisms in the intestine to provide the required physiological quantities and implicated in synthesis of four blood coagulation factors in the liver [7]. The diffeciency of vitamin K in the body is infrequent, but may occur if obstruction of the bile or intestine occurs and in cases of liver disease such as cirrhosis [7]. Diffeciencies are generally accompanied by a decrease in the prothrombin level with an increase in blood coagulation time. At advanced stages, the capillaties may become fragile and hemorrage. Symptoms are reversed by incorporation of vitamin K in diet, except in cases of liver diseases. Also, naftazone which is 1,2-naphthoquinone semicarbazone has been successfully used in the treatment of traumatic or spontaneous hemorrhages. It acts by reducing the fragility of capillaries. Thus it differ from vitamin K in that it does not affect the coagulation time [8]. Anthraquinone and its derivatives are important in applications such as energy conversion and conservation [9-11], electrocatalysis [12], dye and pharmaceuticals [9].

In general, the electrochemistry of quinone/hydroquinone couple has been the subject of many investigators. However the mechanism and kinetics of the exchange of two electrons and two protons are not yet fully understood even for the simplest system, p-benzoquinone/hydroquinone. The sequence of addition of electrons and protons, the kinetics of various steps and the nature of the final product depend on various parameters. The mechanism will of course also depend on the quinone structure as well as the nature and position of substituents.

In connection with the continuing request for a deeper knowledge the conformational properties of DNA and other polynucleotides; the voltammetric behaviour of monomeric nucleosides and nucleotides at charged interfaces were previously investigated in aqueous solutions. Many investigators have reported that various monomeric purine and pyrimidine derivatives are adsorbed at mercury electrodes [13-16]. The DNA bases are particularly interesting subject for study. Their properties have been studied extensively [17] and have found importance in technological and medical applications [18]. Differences in chemistry and electronic properties were investigated [19].

The coumarin compounds are of a large family of organic compounds having a lactone structure and are extensively used in many fields. The parent coumarin is a naturally occuring constituent of many plants. It is mainly used as a substitute for vanillin in pharmaceutical preparations [20]. And it has been used extensively as a flavouring material. Its metabolism in rats and rabbits has been investigated [21]. Umbelliferone which is 7-hydroxycoumarin is the main product of coumarin metabolism in man [20] and it has been used in brain intracellular pH measurements and fluorescent immunoassays [22]. Also, hymecromone, 7-hydroxy-4-methylcoumarin, has to be used as an antispasmodic [23].

1.1 General Background on Microemulsions

Microemulsions are systems of interest for both fundamental studies and many practical applications which is first coined by Schulman and Hoar [24]. Microemulsions are isotropic dispersions of two immiscible fluids, generally oil and water (with or without electrolyte), which are thermodynamically stabilized by the presence of surfactant molecule at the interface [25,26]. The presence of cosurfactant such as a short chain alcohol is critical in reducing the interfacial tension between the droplets and the continuous phase to near zero.

Micelles are dynamic aggregates of amphiphilic or surfactant molecules possessing both hydrophilic and hydrophobic character [27]. A measure of the growth of the field can be obtained from the existing critical micellization concentration (CMC) data. 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 [28,29] of surfactant solutions, if plotted against the concentration, appear to change at a different rate above and below this range. By extrapolating the loci 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 approximate significance of CMC is that it is the equilibrium concentration where surface chemistry ends and colloid chemistry begins. And particles ranging in size from one micron to one millimicron [30].

Microemulsions are to be distinguished from coarse emulsion by their thermodynamic stability [31-37] and by their extremely small sizes, in the range of 50-500

A° versus a typical diameter of one micron (10,000 angstroms) for coarse emulsions [38].

The phase behaviour and microstructure of microemulsion depend on several parameters as observed in numerous thermodynamic studies [37,39]. Such parameters include surfactant type and concentration, cosurfactant type and concentration, electrolyte type and concentration, temperature and pH. The microemulsions can have different structural organization. Water-rich systems called oil-in-water (O/W) microemulsions, having oil droplets surrounded by the interface, which diffuse in a continuous phase of water and referred as to a lower-phase microemulsion. Similarly, oil-rich systems (W/O) microemulsions, having water droplets, surrounded by the interface, which diffuse in a continuous phase of oil and referred to as upper-phase microemulsions. A microemulsion which coexists with both an excess oil and an excess aqueous phase at intermediate salinities (called a middle-phase microemulsion) does not have a distinct phase continuity and is often referred to as bicontinuous [40].

Microemulsions also fall into three classifications by their surfactant charge. Surfactants can be ionic (either anionic or cationic), zwitterionic and nonionic. In such systems, because of microscopic heterogeneity both polar and non-polar compounds can be solubilized due to the simultaneous presence of aqueous and non-aqueous domains.

The literature survey on microemulsions is quite encompassing and has recently been reviewed by Friberg [39] and Holt [37]. The most common tools which have been used to characterize microemulsions include quasielastic light scattering [41-45], NMR [46,47], small angle x-ray [48-50] and neutron scattering [50-52], flourescence spectroscopy [53,54], and ultracentrifuge [55].

Model microemulsion systems which contain pure components have been developed by several authors [56-63]. Chou and Shah [41] investigated the effect of various electrolyte on solubilization in an oil continuous microemulsion containing a petroleum sulfonate as surfactant and found solubilization to be maximal at particular electrolyte concentrations.

Qutubuddin [57] has developed both pH-independent and pH-dependent systems [56,57] contains an alkyl aryl sulfonate as the surfactant while the pH-dependent systems [59] contain oleic acid as the surfactant. The size and charge of the microemulsion droplets have been measured by Qutubuddin et al. [41] using electrophoretic laser light scattering. Also, the effects of additives like polymers on the phase behavior of microemulsion has been investigated by Qutubuddin et al. [65] and is of interest to applications in enhanced oil recovery where aqueous polymer solution is used to push the surfactant slug.

Numerous theoritical studies have been performed in attempts to understand the equilibrium structure of microemulsions. Winsor's [66] assumed that microemulsion structure depends on the natural curvature of the surfactant layer formed at the water/oil interface. And postulated that the 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}. According to this approach, when (E_{lo}/E_{hw})<<1, the natural curvature of the surfactant layers favors formation of small oil droplets in water. However, if the ratio (E_{lo}/E_{hw})>>1, an upper phase microemulsion coexists with an excess aqueous phase. As the ratio approaches unity, the natural curvature of the surfactant layers tends to decrease and bicontinuous structures may exist.

Schulman et al. [67] have 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 [68] 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 are useful in such diverse areas as tertiary oil recovery [69,70], biomedical applications [71], and as media for specialized reactions [72,73]. Other areas in which the application of microemulsions is being considered are polymerization [74,75], precious metal recovery, targetted drug delivery, coating industries [76,77], and advanced fuel technology [78,79].

1.2 Electrochemistry in Microemulsion

Electrochemical methods offer a simple and convenient method for characterizing microemulsion microstructure with greater simplicity and the same versatility as NMR. With electrochemical techniques the diffusion coefficient of an electroactive probe will reflect the self diffusion of the phase in which the probe resides [80-82]. In addition, electrochemical techniques can also be used to study redox and related chemical reactivity in the microheterogeneous environment of microemulsions [81-84]. Diffusion coefficients of micelles and microemulsions can be measured by a variety of electrochemical techniques. Such measurements provide qualitative insight into the interactions of probes with the discontinuous pseudophase. These interactions include surface and double-layer electrostatic interactions, hydrophobic solvation and partitioning. Changes in such interactions that accompany microstructural transitions in microemulsions are qualitatively revealed by electrochemistry diffusion measurements, with good agreement with NMR and quasi-elastic light scattering studies of such systems.

Any electrochemical techniques that allow the determination of the diffusion coefficient of an electroactive substance can, in principle, be used for measuring diffusion in micelle and microemulsion systems. The informations obtained depend on the nature of the electroactive probe, its relative compartmentalization (partitioning) between the continuous and discontinuous pseudophases, and interactions with the interfacial surfactant. Electrochemical techniques that have been used for such studies include polarography [85-89], cyclic voltammetry [90-95], rotating disk voltammetry [95-101], chronoamperometry/chronocoulometry [91,102], and chronopotentiometry. The advantages of these electrochemical techniques are as follows:

(1) The techniques are inexpensive compared to other techniques.

(2) Fast and relatively easy characterization is possible.

(3) No physical properties required except viscosity (which is necessary for calculating the droplet size in any technique). While in other techniques the knowledge of some property

is needed, such as the refractive index of the continuous phase in the case of light scattering.

(4) The electrochemical approach provides self diffusion coefficient while other methods give self diffusion and/or collective diffusion.

(5) Opaque systems can be characterized.

1.3 Literature Survey on Electrochemistry in Microemulsion

1.3.1 Diffusion in conductive microemulsions

The literature survey of electrochemical investigations in microemulsion media is rare since this technique is recently applied to microemulsion systems. Mackay and co-workers [35] have been first to suggest that electrochemical techniques can be used to obtain information about the microstructure of microemulsion. Diffusion coefficients of a water-soluble probe, which have been subsequently measured by Mackay and co-workers in several systems using dc-polarography, were in agreement with those determined from quasi-elastic light scattering (QELS) and were used as evidence for the microdroplet structure [80]. The same authors reported that the diffusion coefficient value (D') of oil soluble probe (1-dodecyl-4-cyanopyridinium ion) was independent of the amount of water in the range from 35-65% (bicontinuous microemulsion) in sodium cetylsulfate (SCS)/water/pentanol/octane system. They used 1-dodecyl-4-cyanopyridinium ion as an effective probe for diffusion measurements of oil droplets in octane/cetyltrimethyammonium bromide (CTAB)/1-butanol/water microemulsions at high water content. Values of D' obtained by polarography were in excellent agreement with those from QELS [80]. Whereas for SCS and CTAB microemulsions with water content, agreement of polarographic D' values with QELS was not as good. This attributed to polydispersity, which is reflected in different ways by the two different methods. Polarography provides apparent self-diffusion coefficients, while QELS can give a self-diffusion coefficient, a collective diffusion coefficient, or a combination of both.

Qutubuddin et al. [95] applied two electrochemical techniques, cyclic voltammetry and rotating disk voltammetry, to characterize oil-in-water microemulsions of hexadecyltrimethylammonium bromide. The diffusion coefficients of microemulsion droplets were determined using ferrocene, and the obtained values were compared with those measured from quasi-elastic light scattering experiments. The observed differences between electrochemical and light scattering measurements are due to the different modes of diffusion probed by both techniques.

Dayalan et al. [103] reviewed the measured diffusion coefficients of ferrocene in micellar and microemulsion systems of CTAB, SDS and DTINS electrochemically. They studied the effect of probe partitioning equilibria, kinetics and pseudophase structure on the apparent diffusion coefficients.

George and Berthod [104] have been reported a number of diffusion studies using electrochemical measurements in microemulsion media. Methylene chloride/sodium p-octylbenzenesulfonate/1-pentanol/water systems were used in this investigation. The diffusion coefficient (D') for oil soluble 10-methylphenothiazine is increased and that for water-soluble hydroquinone is decreased as the fraction (ϕ) of oil content is increased. These data were used to infer a large bicontinuous region in the center of the phase diagram. Electrochemically measured diffusion of water soluble hydroquinone and oil soluble ferrocene was obtained at a series of compositions of microemulsions of brine/SDS/dodecane with 1-pentanol or 1-heptanol as cosurfactants [105]. D'-values were shown to be consistent with conductivity data, microviscosity and polarity estimated by flouresence probe studies.

1.3.2 Diffusion studies with microelectrodes

With W/O microemulsions the continuous phase is of neat oil and this microemulsion type is quite resistive. The iR drop is of large magnitude, therefore it is impossible to obtain measurements with conventional-sized electrodes. However, microelectrodes with dimensions in the µm range are nearly unaffected by iR drop and can be used to study diffusion in highly resistive systems. Chen and Georges [106] first used steady-state microelectrode voltammetry to study diffusion in W/O microemulsion systems. They used ferrocene to probe diffusion in the oil phase of SDS/dodecane/1-pentanol/water systems. The diffusion coefficient of ferrocene reflected the microviscosity of the oil phase, rather than the bulk viscosity of the microemulsion.

1.3.3 Partitioning and equilibria in microemulsions

The distribution of solutes between aqueous and organic domains in colloidal systems is of importance in pharmaceutical, cosmetic, food, photographic, and other industries[107-111]. The dispersed phase in surfactant systems like micellar solutions and microemulsions can not be isolated from the continuous phase without drastically affecting the morphology. Therefore, the measurement of the distribution coefficient (P) for partitioning into the dispersed phase in such systems can not be made by normal analytical methods applicable to macroscopic two-phase systems. The distribution in colloidal systems will be generally different from macroscopic two-phase systems due to the modifying effects of the interface. Qutubuddin et al. [101] determined the distribution coefficients of electroactive solutes between aqueous and organic domains in microemulsions using cyclic and rotating disc votammetry. The apparent distribution coefficients for ferrocyanide ion and substituted *para*-phenylenediamines [4-amino-3-methyl-N-ethyl-N-(β-sulfoethyl)aniline (PPD1) and 4-amino-3-methyl-N,N-diethylaniline (PPD2)] in oil-in-water microemulsions of cetyltrimethylammonium bromide (CTAB) and octadecyldimethyl betaine (C_{18}DMB) were determined and discussed. The authors converted the measured diffusion data to distribution coefficients (P). These P-values were shown to be a lower bound on the actual distribution coefficients as a consequence of neglecting probe-droplet kinetics near the electrode. And they reported that ferrocyanide ion is very weakly bound to CTAB-coated oil droplets. The order of binding was ferrocyanide<<PPD1<<PPD2, with the same binding order of PPD1 and PPD2 in C_{18}DMB microemulsion. Mackay et al. [112] studied the effect of probe partitioning on the electrochemical formal potentials in microheterogeneous solutions using cyclic voltammetry and chronocoulometric techniques. They used ferrocene, methyl viologen and ferricyanide probes to demonstrate 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. They related the shift in formal potential with microemulsion composition are due to changes in both partitioning constants and diffusion coefficients.

The diffusion coefficients of ferricyanide and cadmium ions were measured polarographically [113] in ionic microemulsions of cetyltrimethylammonium bromide. 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. Cd(II) has been shown to be bound at cetyltrimethylammonium bromide interface, presuming the formation of cadmium bromide complex anion. Non-ionic oil in water microemulsions has been shown to exhibit percolation behaviour.

1.3.4 Electrochemical reactions in microemulsions

Iwunze et al. [114] studied the electrochemical behavior of water-soluble ruthenium(III) hexamine, ferrocyanide, and vitamin B_{12}, as well as oil-soluble ferrocene and polycyclic aromatic hydrocarbons (PAH's) in bicontinuous microemulsions of didodecyldimethylammonium bromide (DDAB)/dodecane/water. They found the electrode processes take place quasi-reversible and the obtained results were in a good agreement with simulated voltammograms assuming the bicontinuous medium was homogeneous. Diffusion of the probes did not reflect the high bulk viscosities (19-38 cp) of the DDAB microemulsions. Also, hydrophilic ions diffused at rates characteristic of the aqueous phase; and non-polar molecules diffused at rates similar to the self-diffusion of oil in the oil phase.

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

Garcia et al. [115] recently reported a coulometric initiation of acrylamide polymerization in Aerosol OT/toluene/water (water-in-oil) inverse microemulsions. They overcomed the ohmic resistance by using Pt/Nafion solid polymer electrode (SPE). The SPE is used to separate the inverse microemulsion from an aqueous electrolyte phase. Polymerization was initiated by constant potential electrolytic reduction of $K_2S_2O_8$ (radical initiator) in the inverse microemulsion. The microemulsions used were characterized by microelectrode voltammetry on a variety of electroactive probes.

Garcia et al. [116] reported also 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 (from) Pt ultramicro-electrodes is retarded and above which electron transfer is greatly facilitated. This threshold phenomena attributed to interfacial surfactant packing. Kamau et al. [107] studied the electrochemical catalytic reductions of 1,2-dibromobutane (DBB), trans-1,2-dibromocyclohexane (t-DBCH), and trichloroacetic acid (TCA) mediated by nickel and copper phthalocyaninetetrasulfonates (MPcTS). Bicontinuous microemulsion of didodecyldimethylammonium bromide (DDAB)/dodecane/water and isotropic acetonitrile/water were used as media for this investigation. MPcTS mediators were adsorbed to glassy carbon cathodes from the didoecyldimethylammonium bromide (DDAB) and from acetonitrile/water. The catalytic efficiencies measured by cyclic voltammetry and square wave voltammetry showed that TCA is more reactive in isotropic solvents but DBB and t-DBCH were more reactive in microemulsions.

Generally, surfactants have been widely used as brighteners in the electroplating industry [118] and have promising roles in advanced battery design [119]. Surfactants such as gelatin and Triton X-100 began to be used routinely in electroanalytical chemistry to supress 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 [120-122]. And it is known that adsorption of surfactants on the electrode can have large effects on the kinetics of heterogeneous electron transfer reactions at the DME. A related discovery led to the greatest commercial success of industrial organic chemistry, the electrolytic production of adiponitrile, the precursor to hexaethylenediamine in the manufacture of Nylon 66 [123].

Manuel Baizer [124] reported that acrylonitrile can be electrochemically dimerized to adiponitrile at low cost in concentrated aqueous solutions of tetraethylammonium p-toluenesulfonate (TEATS).

Many microheterogeneous systems, including micelles, microemulsions, vesicles, and polymer films, are of current interest as electrochemical media [125-128]. Since the reagents are localized (in either the oil or water phase), the effective local concentrations are increased. This can increase reaction rates [125,129,130].

Many investigators have demonstrated that coulombic and hydrophobic interactions with surfactants can stabilize various electrochemically produced ion radicals [131]. Electrochemical methods have been used for controlling electrochemical reactions with surfactants as well as aggregate characterizations [132-134]. And novel work was being done with surfactant microstructures to control chemical and photochemical reactions. Recently a microemulsion polymerization technique was used to form a porous non-conducting matrix [135]. The microemulsion is prepared using a surfactant and two monomers, one hydrophilic and the other hydrophobic. Polypyrrole was then electropolymerized into the non-conducting polymer matrix. The surfactant affects the pyrrole electropolymerization and the electrochemical properties of the conductive polymer composite.

Phani et al. [136] studied the electropolymerization of polyparaphenylene in microemulsion medium. The morphology and crystallinity character of the film depends on the film thickness, cycling potential and surfactant. From X-ray diffraction, PPP film prepared without surfactant is amorphous and the crystallinity goes from 100% crystalline into a little crystalline on increasing film thickness.

1.4 Background on Electrochemical Techniques

1.4.1 Cyclic voltammetry (CV)

Cyclic voltammetry is often the first experiment performed in an electrochemical study of a chemical compound, a biological material, or an electrode surface. Its capability for rapid observing the redox behavior over a wide potential range is the main advantage. The resulting voltammogram is analogous to a conventional spectrum in that it conveys information as a function as of an energy scan. Cyclic voltammetry has been employed using stationary electrode in studies of mechanisms of electrode processes. It has been found to be practically useful in investigations of mechanisms of oxidation and reduction of a number of organic substances [137-141]. 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 currents are observed, $E_{p,a}$ and $E_{p,c}$; respectively; information on reversibility or irreversibility of the system and on chemical reactions accompanying electrode processes can be obtained. Extensive treatment of the theory of kinetic and adsorption currents has been presented by Shain et al. [142,143]. And the theory of stationary electrode voltammetry has been presented by Nicholson and others [144-148].

A cyclic voltammogram is obtained by measuring the current at the working electrode during the potential scan. The potential applied to the working electrode is scanned linearly from an initial value E(i) to a predetermined limit E(f) (known as the switching potential) where the direction of the scan is reversed. The controlling potential which is applied across the working and reference electrodes can be considered as an excitation signal. Where the excitation signal for CV is a linear potential scan with a triangular wave-form. This triangular potential excitation signal sweeps the potential of the electrode between two values E(i) to E(f) (versus reference electrode). At which point E(f) the first cycle is completed and the scan direction is reversed causing the potential to scan back to the orginal potential value E(i). Simply, the potential of the electrode is varied linearly with time in either the positive or negative direction until a switching potential is reached, at this time the direction of potential sweep is reversed and the potential is returned to the original value. 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 in a simple manner to the formal potential of the redox process.

1.4.2 Types of charge transfer reactions

1.4.2.1 Reversible reactions

Consider a simple example of reversible reaction type as described by equation I.1, and assuming that only species A is initially present in solution.

$$A + ne^- \Leftrightarrow B \qquad (I.1)$$

If a very slow linear potential sweep is applied to such a system the voltammogram recorded will appear like a steady state I vs. E curve. It is assumed that, under steady state conditions, as the sweep rate is increased, a peak of increasing height develops. This is due to concentrations above certain distance from the electrode are maintained uniform by natural convection. On the other hand, within the region next to the electrode, known as the Nernst diffusion layer, the concentration gradients are especially linear. For a reversible reaction the ratio C_A°/C_B° is given by the Nernst equation, and hence as the potential is scanned to more negative values the surface concentration of the electroactive species C_A°(reactant) must be progressively decreased. The concentration gradient is thereby increased; subsequently the current also is increased. Eventually, the surface concentration of the reactant approaches zero and the steady state concentration profile can not change further; then the current reaches a plateau value. When the sweep rate is increased, the diffusion layer does not extend as far into solution, and the concentration profile is not yet linear. When the reduction potential of species A is reached, the surface concentration of A decreases from its bulk value in order to satisfy the Nernst equation and for a concentration gradient is seted up. The concentration gradient does not of course remain constant, due to its proportionality of current, but start to decrease owing to diffusion. However, at the same time the electrode potential is still changing, and therefore the surface concentration of A is further decreased until it effectively reaches zero. Once $(C_A)_{x=0}$ reaches zero, the concentration gradient starts to decrease, due to relaxation effect and hence the current flowing must be also decreased. Overall, this behavior gives rise to a peak shaped current-potential response. On reversing the sweep, a significant concentration of species B present near the electrode surface and, indeed, species B continuous to be formed on the reverse sweep until the potential again approaches E_e°. However, as the potential approaches E_e° species B starts to be reoxidized back to species A with a reverse current flows. With changing the electrode potential the surface concentration of B eventually reaches zero, and the current on the reverse sweep will also exhibit a peaked response of opposite sign.

The behaviour of the current during the potential scan is given by the following equation [149]:

$$i = nFAD(\partial C/\partial x)_{x=0} \qquad (I.2)$$

where

i - current, amps

n - electron stoichiometry total

A - electrode surface area, cm^2

F - Faraday constant, coulomb per equivalent

Nicholson and Shain [137] 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:

$$i_p = 0.446nFAC_A(nF/RT)^{1/2}v^{1/2}D^{1/2} \qquad (I.3)$$

where

i_p - peak current, amps.

υ - sweep rate, Volt/sec

or at 25°C equation (I.3) can be given as:

$$i_p=(2.69x10^5)n^{3/2}AD_o^{1/2}\upsilon^{1/2}C_o \qquad (I.4)$$

This expression is called Randles and Sevcik [137] equation.

The criteria for the reversible reactions; the peak potential separation is given by [148-149]:

$$\Delta E_p = E_{p,a} - E_{p,c} = 59/n \text{ mV at } 25°C \qquad (I.5)$$

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 $\upsilon^{1/2}$. The ratio of anodic peak current $i_{p,a}$ to cathodic peak current $i_{p,c}$ [148, 150-152] is given by:

$$i_{p,a}/i_{p,c} = 1 \qquad (I.6)$$

For a reversible electrode process Nernst equation [148] is given as:

$$E_{1/2} = E^o + RT/nF \ln(D_O/D_R)^{1/2} \qquad (I.7)$$

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

$$E_{1/2} = (E_{p(a)} + E_{p(c)})/2 \qquad (I.8)$$

1.4.2.2 Irreversible reactions

Irreversibility means the rate of electron transfer is sufficiently slow (opposite to reversible systems) with respect to the potential sweep rate. Therefore, the surface concentration of A and B can not maintain the Nernstian value. As the sweep rate is increased the rate of mass transport increases and the potential of the 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 irreversible reactions there is no peaks observed on the reverse scan.

The peak current response for irreversible process can be obtained by the solution of the differential equations, applying the same boundary conditions as in reversible systems [142]. The exception is that the concentration of the product species is assumed to be zero. By applying the boundary conditions the peak current can be obtained [142] at 25°C as:

$$i_p = (3.01\times10^5)n(\alpha n_a)^{1/2}C_A D_A^{1/2}\upsilon^{1/2} \qquad (I.9)$$

where

α - transfer coefficient,

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

and other terms have their usual significances.

The peak potential E_p for an irreversible electrode reaction was found to be dependent on sweep rate as given by the following equation [142]:

$$E_p = E_e^o - RT/\alpha n_a F[0.78 - \ln(\alpha n_a FD/k^{o2}RT)^{1/2}] - (RT/2\alpha n_a F)\ln(\upsilon) \qquad (I.10)$$

where

E_e^o - is the standard electrode potential,

k° - is the standard rate constant

i.e. there is about $30/(\alpha n_a)$ mV cathodic shift in the peak potential for every ten-fold increase in sweep rate. This criteria can be used to characterize the irreversible process. The separation of E_p and $E_{p/2}$ is given by the following equation:

$$[E_p - E_{p/2}] = 48/\alpha n_a \text{ mV, at } 25°C \qquad (I.11)$$

In the present work the kinetic parameters, k° and αn_a, of the electrode reaction were calculated using the following equation [153]:

$$E_p = -1.14(RT/\alpha n_a F) + (RT/\alpha n_a F)\ln(k^{\circ}_{f,h}/D^{1/2}) - RT/2\alpha n_a F.\ln(\alpha n_a \upsilon) \qquad (I.12)$$

1.5 Rotating Disk Voltammetry (RDV)

There are many electrochemical techniques in which the electrode moves with respect to the solution; such as rotating disk, rotating ring, streaming mercury and vibrating electrodes. These systems in which the electrode is in a motion or involving convective mass tranport of reactants and products are generally called hydrodynamic methods. The most practical form of an electrode for which a completely rigorous hydrodynamic treatment can be given and easily controlled [154-158], is the rotating disk electrode(RDE). A completely rigorous hydrodynamic treatment has been given by Levich in 1942 [154]. 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 in these methods are much larger than the rate of diffusion; the relative contribution of the effect of mass transfer to electron transfer kinetics is smaller.

The theory of a RDE applies to a thin plane surface so large in diameter that the edges may be neglected with respect to the total surface. This plane is rotated at a constant angular velocity about an axis perpendicular to the plane. As the disk rotates, the adjacent liquid thin layers acquire the rotation motion of the disk. Liquid thus entrained has a tangential velocity and also develops a radial velocity away from the center of the disk, due to the centrifugal force. This flow pattern, which moves liquid horizontally out and away from the center of the disk, requires an upward axial flow to replenish liquid at the disk surface. The general convective-diffusion equation [148] is given by:

$$\partial C/\partial t = D\nabla^2 C - v\nabla C \qquad \text{(I.13)}$$

where ∇^2 is the Laplacian operator and v is a velocity vector represents the motion of the solution. Applying the steady state and boundary conditions, equation I.13 can be simplified as [148]:

$$v_y(\partial C/\partial y) = D(\partial 2C/\partial y^2) \qquad \text{(I.14)}$$

Karman and Cochran obtained the following expression for the velocity vector and given as:

$$v_y = (\omega v)^{1/2}(-a\gamma^2) = -\,0.51\omega^{3/2}v^{-1/2}y^2 \qquad \text{(I.15)}$$

Also, the current i, is the flux at the electrode surface:

$$i = nFAD_o(\partial C/\partial y)_{y=0} \qquad \text{(I.16)}$$

The limiting current conditions obtained when the concentration at the electrode surface approaches zero under mass transfer control. Levich [159] first solved this problem and the Levich equation is given by:

$$i_{(L)} = 0.6205nFA(D^{2/3})(v^{-1/6})(\omega^{1/2})C \qquad \text{(I.17)}$$

where

$i_{(L)}$ - limiting current, amps.

F - Faraday's constant, 96487 coulomb/equivalent

A - electrode surface area, cm^2/sec

ω - angular velocity, rad/sec

ν - kinematic viscosity, gm/cm.sec

C - bulk concentration of electroactive species, $mole/cm^3$

A careful check of the accuracy of the limiting currents over a wide range of rotation rates and as a function of temperature led Gregory and Riddiford [160] to propose an important modification to equation I.17. Using additional terms in the expansion of the particular integral involved; they verified that the numerical constant 0.6205 should be replaced by the quantity:

$$\frac{0.554(Sc)^{-2/3}}{0.8934 + 0.316(Sc)^{-0.36}} \qquad (I.18)$$

where Sc is called a Schmidt number and is equal to ν/D. This correction applies within 1% for Schmidt number ($Sc > 250$). Recently Newson and Riddiford [161] have pointed out that the correction to the Levich equation becomes less important as the Schmidt (Prandtl) number increases. Newman [162] also proposed a better correction for a moderate Schmidt number:

$$i(L) = \frac{0.62048\ Sc^{-2/3}}{1 + 0.2980 Sc^{-1/3} + 0.14514 Sc^{-2/3}} \qquad (I.19)$$

Newman showed that when Schmidt number is higher or equal to 1400; the percentage deviation between equation I.19 and an exact numerical evaluation is less than 0.005%. While the percentage deviation between Levich equation and exact numerical evaluation is within 3%.

It would appear that precise measurements of quantities like D and A values can be determined by measuring the limiting current, i(L), at several rotation speeds, ω. The diffusion coefficient was measured by Landau [163] in $CuSO_4$-H_2SO_4-Glycerol system. The theory of the rotating disk voltammetry technique is reviewed by several authors [164-168], and the current distribution at RDE is well discussed by Newman [167].

The current at a given potential at the RDE; assuming the simple reaction ($A + ne^- \Leftrightarrow B$); (I.1) can be given as:

$$i = i_l \{C - C_{(x=0)}\}/C \qquad (I.20)$$

and the potential is given by the familiar Nernstian voltammetric wave equation:

$$E = E_{1/2} + RT/nF \ln[(i_l - i)/i] \qquad (I.21)$$

where

$E_{1/2} = E^{0'} + RT/nF \ln(D_R/D_O)^{2/3}$

1.5.1 Applicable range for rotation speed (ω)

The equations involved for the RDE will not apply at very small or very large values of rotation speed ω. When ω is small, the hydrodynamic boundary layer [$\delta = 3(\nu/\omega)^{1/2}$] becomes large, and it approaches the disk radius R_1, the approximations $R_1 >> \delta$ will break down. Thus, the lower limit for ω is obtained from the condition that $R_1 >> 3(\nu/\omega)^{1/2}$, that is, $\omega > 10\nu/R_1^2$. Also to achieve a steady-state concentration at the electrode surface($\partial C_0/\partial t = 0$), the rate at which the electrode potential is scanned by volt/sec must be small with respect to ω values. If the scan rate is too large for a given ω, the current-potential response will not have S-shape predicted by Nernst equation [148] but will instead show a peak as in linear scan voltammetry at a stationary electrode.

The upper limit for ω is governed by the onset of turbulent flow. This occurs at the rotating disk electrode at a Reynolds number, R_e(critical) is about 2×10^5 [169,170]. Where R_e(critical) is defined as:

$$R_e(\text{critical}) = \omega(R_1)^2/\nu$$

The condition for nonturbulent flow is that $\omega < 2\times10^5\nu/R_1^2$. It was found practically that, the maximum rotation rates are frequently 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 < ω < 10,000 RPM ".

In our case of study the upper limit of ω was restricted to 3000 RPM because beyond this speed, the foaming of microemulsions starts. And since the boundary layer diffusion thickness δ > microemulsion droplet size >> probe size, RDV can be applied for characterization of microemulsions.

1.6 Chronocoulometry (CC)

Chronocoulometry is one of the classical electrochemical techniques that enjoys frequent usage 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 has been as extremely valuble technique for direct measurement of the adsorption of electroactive species [171-176]. This technique was first popularized by Anson [172] and co-workers. The advantages of chronocoulometry that is easily applied to fast reactions, the measured signal are least distorted by nonideal potential rise and offer 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. And is specially valuable for the study of surface processes at the electrode [171-176].

Figure I.6 shows a typical current potential curve (recorded under steady-state conditions) for the reduction of electroactive species at the electrode surface. No current flows untill 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 the electrode surface by means of a linear diffusion (i.e. unstirred solution, flat electrode). An equation originally derived by Cottrell [171] 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:

$$i = nFAC(D/\pi t)^{1/2} \qquad (I.22)$$

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 [175].

The total charge passing through the electrode process is the integral over time of the two current components [150-153]:

$$Q_{tot} = \int_0^t i(c)\,dt + \int_0^t i(L)\,dt \qquad (I.23)$$

$$Q_{tot} = (2nFAD_o^{1/2}C_o t^{1/2})/\pi^{1/2} + Q_c \qquad (I.24)$$

where Q_c is the interfacial capacitance charge when the electrode potential is stepped from E(1) to E(2). Suppose some of the reactant is adsorbed at the electrode/electrolyte interface while the electrode is resting at potential E(1). When the potential is stepped to E(2) all of the adsorbed reactants will be reduced essentially instantaneously, because they are already present on the electrode surface and require no time to diffuse to the surface. Therefore, the total amount of charge (Q_{tot}) in the presence of adsorbed reactants should involve the extra charge produced by the adsorption (Q_{ads}). The chronocoulometric response will not affected by the adsorption of reactant and the total charge in the presence of adsorption will be given as:

$$Q_{tot} = (2nFAD_o^{1/2}C_o t^{1/2})/\pi^{1/2} + Q_c + Q_{ads} \qquad (I.25)$$

The value of Q_{ads} is directly taken as a measure of the quantity of reactant adsorbed at the electrode surface , and by using Faraday's law the amount of Q_{ads} is given as following:

$$Q_{ads} = nFA\Gamma_o \qquad (I.26)$$

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

Under these conditions the plot of Q_{tot} vs. $t^{1/2}$ (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 necessary 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.25) 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. And 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) [172]. Figure I.2 depicts the potential-, current-, and charge-time response obtained in such a double-potential step experiment. The response of the reverse step under diffusion control is given by the following equation [172-173&177]:

$$Q_r = Q_c + (2nFAD_o^{1/2}C_o[\theta])/\pi^{1/2} + nFA\Gamma_R \qquad (I.27)$$

where,

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

ξ = forward step width, sec

There is no capacitive component in Q_{tot} equation (I.25) in case of double-potential step chronocoulometry because the net potential change is zero. The pair of plots, Q_{tot} vs. $t^{1/2}$ and Q_r vs. θ is extremely useful for quantifying electrode reactions of adsorbed species. The difference in intercepts of the forward and reverse steps provides the adsorbed reactant [172,175] which is in general:

$$\text{Intercept 1 - Intercept 2} = nFA(\Gamma_O - \Gamma_R) \qquad (I.28)$$

In addition to the study of adsorbed species, chronocoulometry can be used to study the homogeneous chemistry of oxidant and reductant [148,176]. Ideally the potential step should be instantaneous. In practice this is not possible, and initial data are therefore distorted. To compensate for this, BAS-100 (Electrochemical Analyzer used in this work) uses only the last 80% of the collective data in calculating slopes and intercepts of the Anson plots.