SUMMARY

SUMMARY

The present thesis deals with microemulsion characterization and microemulsion application as media for electrochemical reactions. The effect of microemulsion as a local environment in comparison to pure aqueous medium on the electrode process, kinetics and thermodynamics were recorded for a model quinone, nucleic acids and for two different series of azo compounds, in both aqueous and microemulsion media.

Also, the charge transfer switching reactions of polypyrrole and polyaniline conductive composites were recorded for polymer composites prepared at different potential steps and different amounts of charge passed during the electropolymerization process. This work comprises three chapters:

Chapter (I) includes an introduction and background on microemulsions and a literature survey on the electrochemical investigations in microemulsion media. Extension of chapter (I) was a background on the electrochemical techniques used in these investigations.

Chapter (II) includes preparation of azo compounds derived from 6,7-dihydroxycoumarin and those derived from 2-hydroxy-6-naphthalenesulfonic acid, instruments and solutions which were used for the measurements using different techniques. It also includes the methods of preparation of nonconductive coatings by microemulsion copolymerization in the presence of SDS and polymerizable surfactant.

Chapter (III) is divided into two main parts. Part (A) includes microemulsion characterization by using different electrochemical techniques and the use of microemulsion and micelles as media in the electrochemical investigation of electrode reactions. It is subdivided into eight parts:

1- Electrochemical characterization of three different microemulsion systems using ferrocene as a standard probe. Cetyltrimethylammonium bromide, CTAB, sodium dodecyl sulphate, SDS and octylphenoxypolyoxyethylene, Triton X-100 model surfactants were used in this investigation. Cyclic voltammograms of 1 mM of ferrocene were recorded in the different surfactant systems. It was found that ferrocene has only a single redox couple of peaks. The peak separation ΔE_p is around 60 mV indicating a single electron transfer. The peak current ratio of $I_{p,a}/I_{p,c}$ was found not to exceed 1.15 indicating that adsorption of surfactants on the electrode surface is negligible and it was confirmed by using the double potential step chronocoulometry technique. The plots of the anodic peak current ($I_{p,a}$) versus $\upsilon^{1/2}$ showed linear correlations passing through the origin indicating that the electrode process is diffusion controlled. The apparent diffusion coefficients of microemulsion droplets were determined from the slope. By using the Stoke's-Einstein equation, the radius of microemulsion droplets was calculated to be 123, 44 and 72 A° for CTAB, SDS and Triton X-100, respectively. These results were confirmed from the rotating disc electrode study in these media. The effects of temperature and hydrocarbon content on the microemulsion droplet size were determined. It was found that the size of microemulsions is increased on increasing the percentage of n-octane, while it decreased with increasing temperature..

2- The electrochemical behaviour of a model quinone 1-amino-9,10-anthraquinone (1AAQ) was observed in micelles and microemulsions of three different surfactant types as well as in aqueous solution using cyclic voltammetry. The voltammograms showed a single reduction step in all media, except in CTAB micelles a shoulder appears and becomes a peak on increasing the sweep rate. In general, the peak separation ΔE_p is 30 mV at lower sweep rates indicating a 2-electron transfer and increases on increasing sweep rate up to 55 mV. Generally, the ratio of peak current ($I_{p,a}/I_{p,c}$) is less than unity in microemulsions and much less in micellar solutions. These electrochemical results indicate that a chemical reaction has to take place, the disproportionation of $1AAQ^{-\cdot}$ anionic radical to the original quinone (1AAQ) and hydroquinone ($1AAQH_2$) . Differences in E_p, ΔE_p and the $I_{p,a}/I_{p,c}$ values is explained in terms of stabilization mechanisms. Stabilization is imparted by electrostatic and/ or hydrophobic interactions. The surfactant present affects the stability of $1AAQ^{-\cdot}$ and thus the equilibrium of the disproportionation reaction to different extents. It was found that CTAB stabilizes 1AAQ more than SDS and Triton X-100 by electrostatic interactions and tends to inhibit the disproportionation of 1AAQ. SDS and Triton X-100 systems also stabilize 1AAQ by surface interaction. This leads to a slower disproportionation of 1AAQ and the reduction of 1AAQ becomes chemically quasi-reversible with a net transfer of two electrons. Diffusion coefficient values of oxidized and reduced forms indicate the partitioning of 1AAQ between oil droplet, surfactant film and aqueous domain.

There is no adsorption on the electrode in micellar solutions and microemulsions compared to aqueous media. This was confirmed by chronocoulometry since the amount of adsorption of 1AAQ on the electrode surface was found to be in the order of 10^{-12} moles which is negligible. These results confirmed that the reactivity of the quinoid moiety in biological systems is critically dependent on its location and the surrounding environment.

3- The cyclic voltammograms of nucleic acids (adenine and cytosine) were recorded in micelles and microemulsion media of three different surfactant types and in aqueous solution. CTAB, SDS and Triton X-100 model surfactants were used. The voltammograms showed a single reduction step for adenine and cytosine in all media. The absence of any anodic peaks in the reverse scan as well as the values of αn_a indicate the irreversible nature of the electrode process. The peak potential (E_p) displayed a cathodic shift on increasing the sweep rate which further confirms the irreversible reduction process. Complications observed in aqueous media due to adsorption and catalytic activity on the electrode surface were eliminated in microemulsions. It is postulated that surfactant stabilization of reactant, intermediate and products purine and pyrimidine moities were partitioned into microemulsions.

4- The cyclic voltammograms of two series of azo compounds [coumarin azo-compounds (series I), and Schiffer azodyes (series II)] were recorded in microemulsion media of three different surfactant types (CTAB, SDS and Triton X-100) using a GCE. The CV was also observed using a HDME in aqueous buffered solutions of different pH values containing 40% (v/v) ethanol for compounds of series (I) and in pure aqueous solution for compounds of series (II). The voltammograms showed a single reduction step in all microemulsions and aqueous solutions. The peak potential displayed cathodic shift on increasing both sweep rate and pH of solution, indicating that irreversible reduction takes place and the reduction includes the consumption of protons. The plots of peak current (I_p) versus $\upsilon^{1/2}$ showed linear correlations intersecting the origin in microemulsion media indicating that the electrode process is diffusion controlled. However, such plots for pure aqueous buffered solutions showed some adsorption on the electrode. The values of the transfer coefficient (α) were obtained from the E_p-$\ln(\upsilon)$ plots in all media for the compounds of the two series and were found to be less than unity indicating the irreversible nature of the electrode process.

5- The different kinetic parameters of the various electrode reactions and the substituent effect on the reduction mechanism were determined. It was found that the heterogeneous rate constant ($k^{\circ}_{f,h}$) in cationic CTAB systems is higher than in aqueous solutions or anionic, SDS, and nonionic, Triton X-100 systems.

6- Thermodynamic parameters, such as $\Delta G^{\#}$, $\Delta H^{\#}$ and $\Delta S^{\#}$ of the electrode reactions were determined for cytosine, adenine and coumarin azodyes in both aqueous and microemulsion media. Also, the activation energy (E_a) of the reduction of 1AAQ was determined. Inspection of the values revealed a positive enthalpy changes indicating the irreversible nature of the electrode process. Negative entropy change means an ordered electrode reaction becomes less ordered on increasing temperature. Values of the activation energy indicate that the electrode reaction in CTAB systems is less ordered compared to Triton X-100 and SDS systems.

7- The electrode mechanisms of 1AAQ, adenine and cytosine as well as the two series of dyes were determined from the obtained data and the total number of electrons determined from the controlled potential electrolysis and found to be 2 in case of 1AAQ, 4 in case of adenine, 3 in case of cytosine and 4 for the azodye compounds of the two series.

8- The effect of complex formation of Schiffer azodye compounds on the voltammetric behaviour of Cu(II) and Zn(II) ions was recorded. The stoichiometry of complexes formed in solution were determined as well as their stability constants.

Part (B)

Part (B) includes the preparation of conductive composite polymers such as polypyrrole and polyaniline films. The method of preparation of conductive composites is a two-step process combining chemical and electrochemical methods. The chemical step includes the copolymerization of MMA/HEA from SDS microemulsion and MMA/AA in the presence of Na 11-AAU to obtain hydrophilic porous nonconductive coatings.

The second step is electrochemical polymerization of either pyrrole or aniline monomer through the noncondutive coating in the presence of a dopant anion such as 0.1 M of either 1,3-benzenedisulfonate or toluenesulfonate in case of pyrrole or 1 M of perchloric acid in case of aniline electropolymerization.

The chronoamperometric responses of electropolymerized films obtained potentiostatically at 650, 800, 1000, 1500 and 2000 mV indicate overoxidation for conductive polymer composites prepared at potentials > 1000 mV. Cyclic voltammograms were recorded for polypyrrole composite films prepared at different potential steps by passing 30 mC. At potentials less than 800 mV, the anodic peak currents of polypyrrole composite films incorporating either toluenesulfonate or 1,3-benzenedisulfonate showed linear dependence on the sweep rate indicating that the rate controlling step is the electron transfer process from or into the polymer chains.

In general, an emperical correlation was used to determine the rate controlling reaction of the polymer composites by studying the effect of the amount of charge passed during electropolymerization on the cyclic voltammetric responses of polymer composite films prepared by applying different potential steps.

The thermal and mechanical properties of the polymer coatings were discussed and the morphology of different polymer composites was observed by scanning electron microscopy (SEM). The effects of potential of polymerization and the amount of charge passed on the morphology and sheet resistivity were determined.