SUMMARY

The present thesis deals with electrochemical investigations of micelles and microemulsions characterization and their applications as media for electrochemical reactions. The effect of micelles and microemulsion systems as local micro environment as well as pure aqueous medium on the electrode process was recorded for four model naphthoquinones in both aqueous, micelles and microemulsion media of three different surfactants. This work comprises three chapters:

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

Chapter (II) include instruments and solutions which were used for the measurements using different techniques. It also includes phase behaviour of both AOT and C_{18}DMB microemulsions.

Chapter (III) is divided into two main parts. part (A) includes the characterization of micelles and microemulsions by using three different eletrochemical techniques. It is subdivided into two parts:

1- Electrochemical characterization of AOT micelles and micro-emulsion systems using ferrocene as a standard probe. Bis (2-ethyhexyl)sulfosuccinate (AOT), model anionic surfactant was used in this investigation. Cyclic voltammograms of different conentrations of ferrocene were recorded in AOT micelles. It was found that ferrocene has only a single redox couple of peaks, the peak sepration 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 the electrochemical behavioure of ferrocene is completely reversible and surfactant adsorption on the electrode surface is negligible as 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. Both cyclic voltammetry (CV) and rotating disk voltammetry (RDV) were used successfully for the determination of the critical micelle concentration (CMC). The critical micelle concentration (CMC) was found to amount 5.05×10^{-4} M in 0.1 M NaCl, 25°C. The rotating disk voltammetry experiments were used to determine the diffusion coefficients of AOT micelles. The diffusion coefficients obtained directly from the experiment represent apparent values. These apparent diffusion coefficients of ferrocene are sum of diffusion coefficient of ferrocene present in the aqueous phase and that present in micelles. So correction can be made to obtain a better estimate of the actual micelle diffusion coefficient The corrections of these values of diffusion coefficient obtained from RDV were done using two methods of treatments slow rate which termed as zero-kinetics and fast-rate. The apparent and corrected diffusion coefficients D_a and D_d were sharply decreased before the critical micelles concentration then becomes nearly constant as the surfactant concentration is increased. Inspection of the values of D_d indicated that the micellar size is becoming nearly constant on increasing the surfactant concentration and the morphological features revealed that AOT is spherical in shape and not rod-like.

The effect of salt concentration on the diffusion coefficient of AOT micellar solutions was studied. It was found that the micellar diffusion coefficient (D_d) is gradually decreases while the half–wave potential $E_{1/2}$ for the oxidation of ferrocene in micellar solutions increases linearly with increasing salinity.

Cyclic voltammograms of ferrocene were recorded in AOT microemulsion. The voltammmograms show one anodic and one cathodic peak on the anodic and cathodic sweeps. The anodic to cathodic peak current ratios ($I_{p,a}/I_{p,c}$) does not exceed 1.074, which indicate the reversibility of the electrode process and confirmed that there is no adsorption on the electrode surface. The peak potential seperation ΔE_p is almost around the theoritical value for one-electron transfer 60 mV. 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 slopes of the plots. By using the Stoke's-Einstein equation, the radius of microemulsion droplets were calculated to be 44, 115,133 and 188 A°. The effects of probe, salt and surfactant concentration, and hydrocarbon content on the diffusion coefficient and microemulsion droplet sizes were determined. It was found that the size of microemulsions is increased on increasing the percentage of n-decane and on increasing concentration of ferrocene and of NaCl, while it decreased with surfactant concentration. These results were confirmed from the rotating disk voltammetric studies in these media.

2- Electrochemical characterization of octadecyldimethyl betaine (C_{18}DMB) which used as zwitterionic surfactant was studied using CV, RDV and CC. Cyclic voltammograms of different conentrations of ferrocene were recorded in the (C_{18}DMB) micelle. The voltammograms showed a single redox couple of peaks of ferrocene in C_{18}DMB micelle, the peak separation ΔE_p is around 60 mV indicating a single electron transfer. The anodic peak current, $I_{p,a}$ and the cathodic peak current, $I_{p,c}$ are almost of equal heights and the ratio of $I_{p,a}/I_{p,c}$ does not exceed 1.095 at different sweeps in all media. Adsorption of surfactant 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 determination of the critical micelle concentration (CMC) was done using both cyclic voltammetry (CV) and rotating disk voltammetry (RDV). The CMC was obtained at 0.2% (wt./wt.) of C_{18}DMB in 0.1 M NaCl at 40°C. The correction of the diffusion coefficients which obtained from rotating disk voltammetry experiments was made to obtain a better estimate of the actual micelles diffusion coefficient. The apparent diffusion coefficients of ferrocene are corrected using two methods of treatments slow rate and fast-rate. The apparent and corrected diffusion coefficients D_a and D_d were sharply decreased before the critical micelles concentration then becoming nearly constant as the surfactant concentration is increased. Inspection of the values of D_d indicated that the micellar size is becomes nearly constant by increasing the surfactant concentration and the morphological features revealed that C_{18}DMB is spherical in shape and not rod-like. The effect of salt concentration on the diffusion coefficient of C_{18}DMB micellar solutions, was studied. It was found that the micellar diffusion coefficient (D_d) is gradually decreases while the half-wave potential $E_{1/2}$ for the oxidation of ferrocene in micellar solutions increases linearly with increasing salinity.

The cyclic voltammmograms recorded in microemulsion system show one anodic and one cathodic peak on the anodic and cathodic sweeps. The reversibility of the electrode process can be indicated from the anodic to cathodic peak current ratios ($I_{p,a}/I_{p,c}$) which does not exceed 1.095. The peak potential separation ($\Delta E_p = (E_{p,a} - E_{p,c})$) values were found almost around the theoretical value for one-electron transfer ~

60mV. 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. On using Stoke's-Einstein equation, the radius of microemulsion droplets was calculated. The effects of probe, salt and surfactant concentration, and hydrocarbon content on the diffusion coefficient and microemulsion droplet sizes were determined. It was found that the size of microemulsions is increased on increasing the percentage of n-decane and on increasing concentration of ferrocene and of NaCl, while it decreased with surfactant concentration. These results were confirmed from the rotating disk electrode study in these media.

Part (B)

This part includes the application of micelles and microemulsion as media in electrochemical investigations. It subdivided into four parts:

1- The electrochemical behaviour of 1,4-naphthoquinone (1,4NAQ) was recorded in micelles and microemulsions of three different surfactant types as well as in pure aqueous solution using cyclic voltammetry (CV), rotating disk voltammetry (RDV) and chronocoulametry (CC). The voltammograms displayed one cathodic peak on the cathodic scan and one anodic peak on the reverse scan in all micelles and microemulsion media, except in C_{18}DMB micelles it displayed two oxidation peaks of almost equal heights. The peak potential separation ΔE_P is very close to 30 mV at very small sweep rates in CTAB microemulsion system and around the theoritical value for 2-electron transfer process. In other media, the peak potential value increased on increasing the sweep rate which leads generally to the fact that the electrochemical-chemical-electrochemical

(ECE) reaction nature. Protonation of the anion radical generally leads to a disproportionation reaction.The peak currents on the cathodic and anodic branches of sweep are slightly different and the ratio $I_{p,a}/I_{p,c}$ is slightly less than unity in micelles and microemulsion systems. These results indicated the very weak adsorption contribution. The values of the apparent diffusion coefficients indicate the partitioning of 1,4-naphthoquinone between oil droplet, surfactant film and aqueous domain.

The rotating disk voltammograms of 1mM of 1,4-naphthoquinone showed a single reduction wave in pure aqueous and in micelles and microemulsion media. Except, in C_{18}DMB micelles it showed two waves, It was found that on increasing the rotation speed there is a negative shift (~20 mV) in the half-wave potential ($E_{1/2}$) indicating the chemical reversibility. The plots of i_l versus $\omega^{1/2}$ in all media showed linear correlations passing through the origin. This behaviour indicates that the reduction process takes place under mass transfer control. The slopes of these plots were used to estimate the apparent diffusion coefficients in various media.

The chronocoulometry technique was used to estimate the amount of adsorbed reactant species on the electrode surface and was found to be in the order of 10^{-9} mole/cm^2.

2- The electrochemical behaviour of 2-methyl-1,4-naphthoquinone (2-ME-1,4NAQ) was recorded in micelles and microemulsions of three different surfactant types as well as in aqueous solution. CTAB, AOT and C_{18}DMB model surfactants were used. The cyclic voltammograms displayed one cathodic peak on the cathodic scan and one anodic peak on the reverse scan in all micelles and microemulsion media, except in CTAB microemulsion it displayed two reduction peaks at small scan rate of almost equal heights. Whereas, in C_{18}DMB micelles it displayed two oxidation peaks of almost equal heights. The peak potential separation ΔE is 30 mV at very small sweep rates in aqueous and CTAB micellar solutions and around the theoretical value for 2-electron transfer process. In other media, the peak potential seperation ΔE_P is greater than the theoritical value which leads generally to the fact that the electrochemical-chemical-electrochemical (ECE) reaction nature. Protonation of the anion radical generally leads to a disproportionation reaction. The peak currents on the cathodic and anodic branches of sweep are slightly different and the ratio $I_{p,a}/I_{p,c}$ is slightly less than unity in micelles and microemulsion systems. The plots of the cathodic peak currents ($I_{p,c}$) as well as the anodic one ($I_{p,a}$) versus $\upsilon^{1/2}$ for 2-methyl-1,4-naphthoquinone in micelles and microemulsion of different surfactant systems as well as in pure aqueous showed linear correlations almost passing through the origin. This behoviour confirming that the electrode reaction is mainly controlled by diffusion with slight adsorption contribution. The values of the apparent diffusion coefficients indicate the partitioning of 2-methyl-1,4-naphthoquinone between oil droplet, surfactant film and aqueous domain.

The rotating disk voltammograms of 2-methyl-1,4-naphthoquinone were recorded in micelles and microemulsion media of three different surfactants as well as in pure aqueous solution. The recorded voltammograms of 2-methyl-1,4-naphthoquinone displayed single reduction wave in pure aqueous and in micelles and microemulsion media. It was found that on increasing the rotation speed there is a negative shift (~20 mV) in the half-wave potential ($E_{1/2}$) indicating the chemical reversibility.

The amount of adsorption of 2-methyl-1,4-naphthoquinone on the electrode surface was estimated from the chronocoulometry technique and was found to be in the order of 10^{-8} to 10^{-9} mole/cm^{2}.

3- The cyclic voltammetric behaviour of 2-hydroxy-1,4-naphthoquinone (2-OH-1,4NAQ) was recorded in micelles and microemulsions of three different surfactant types as well as in aqueous solution. CTAB, AOT and C_{18}DMB model surfactants were used. The voltammograms displayed two cathodic peaks on the cathodic scan and two anodic peaks on the reverse scan in all micelles and microemulsion media, except in C_{18}DMB micelles it displayed one redox peak, and in C_{18}DMB microemulsion showed one oxidation and two reduction peaks. ΔE_P is 30 mV at very small sweep rates in CTAB micelle for the first redox peak and around the theoretical value for 2-electron transfer process. In other media, the peak potential value which leads generally to the fact that the electrochemical- chemical- electrochemical (ECE) reaction nature. Protonation of the anion radical generally leads to a disproportionation reaction.The peak currents on the cathodic and anodic branches of sweep are slightly different and the ratio $I_{p,a}/I_{p,c}$ is slightly less than unity in micelles and microemulsion systems. These results indicated the very weak adsorption contribution. The plots of the cathodic peak currents ($I_{p,c}$) as well as the anodic one ($I_{p,a}$) versus $\upsilon^{1/2}$ for 2-hydroxy-1,4-naphthoquinone in micelles and microemulsion of different surfactant systems showed linear correlations almost passing through the origin,. This behoviour confirming that the electrode reaction is mainly controlled by diffusion with slight adsorption contribution. On the other hand, The plots of the cathodic peak currents ($I_{p,c}$) as well as the anodic one ($I_{p,a}$) versus $\upsilon^{1/2}$ for 1,4-naphthoquinone in pure aqueous solution is deviated from linearity at high sweep rates. This behaviour may be attributed to adsorption on the electrode surface. The slopes of I_p-$\upsilon^{1/2}$ plots were used to estimate the apparent diffusion coefficients of the reduced and oxidized forms of the species D_R and D_O In the present investigation, the ratio $I_{p,a}/I_{p,c}$ is slightly less than unity in micelles and microemulsion systems. These results indicated the very weak adsorption contribution.The slightly smaller ΔE_P (25 mV) in CTAB micelle and about 139 mV in microemulsion for first redox peak compared to that of both AOT and C_{18}DMB micellar and microemulsions shows that the stabilization for cationic surfactants is higher than for anionic and zwitterionic surfactants. This is because the electrostatic effects are generally less in anionic and zwitterionic surfactants than in cationic surfactants. Also, ΔE_P values are close to 30 mV at very slow sweep rates and increase with increasing sweep rates. These characteristics are typical of a reversible charge transfer reaction followed by a slow chemical reaction.

The rotating disk voltammograms of 1mM of 2-hydroxy-1,4-naphthoquinone were recorded in pure aqueous solution as well as micelles and microemulsion systems of three different surfactant types. Cationic (CTAB), anionic AOT and zwitherionic C_{18}DMB surfactants were used in this investigation. The recorded voltammograms of 2-hydroxy-1,4-naphthoquinone displayed two reduction waves in pure aqueous and in micelles and microemulsion media. Except, in C_{18}DMB micelle and microemulsion it displayed a single wave. The plots of i_l versus $\omega^{1/2}$ in all media showed linear correlations passing through the origin. This behaviour indicates that the reduction process takes place under mass transfer control. The slopes of these plots were used to determine the apparent diffusion coefficients in various media.

The chronocoulometric responses of 2-hydroxy-1,4-naphthoquinone were recorded in micellar solutions and microemulsion systems. Values of the amount of adsorbed reactant species on the electrode surface were estimated and were found to be in the order of 10^{-9} mole/cm^2.

4- The cyclic voltammograms of 1,2-napthoquinone-4-sodium sulfonate (1,2NAQ) were recorded in micelles and microemulsion media of CTAB, AOT and C_{18}DMB surfactants and in aqueous solution. The voltammograms displayed one cathodic peak on the cathodic scan and one anodic peak on the reverse scan in all micelles and microemulsion media, except in AOT micelles and C_{18}DMB microemulsion it displayed two oxidation peaks of almost equal heights and two reduction peaks, resvectively. ΔE_P is very close to 30 mV at very small sweep rates in CTAB micelle and microemulsion and AOT microemulsion systems. In other media, the peak potential value which leads generally to the fact that the electrochemical- chemical- electrochemical (ECE) reaction nature. Protonation of the anion radical generally leads to a disproportionation reaction. The peak currents on the cathodic and anodic branches of sweep are slightly different and the ratio $I_{p,a}/I_{p,c}$ is slightly less than unity in micelles and microemulsion systems. These results indicated the very weak adsorption contribution. The plots of the cathodic peak currents ($I_{p,c}$) as well as the anodic one ($I_{p,a}$) versus $\upsilon^{1/2}$ in micelles and microemulsion of different surfactant systems showed linear correlations almost passing through the origin. This behaviour confirming that the electrode reaction is mainly controlled by diffusion with slight adsorption contribution. On the other hand, The plots of the cathodic peak currents ($I_{p,c}$) as well as the anodic one ($I_{p,a}$) versus $\upsilon^{1/2}$ for 1,2-naphthoquinone-4-sodium sulfonate in pure aqueous solution is deviated from linearity at high sweep rates. This behaviour may be attributed to adsorption on the electrode surface. The slopes of I_p-$\upsilon^{1/2}$ plots were used to estimate the apparent diffusion coefficients of the reduced and oxidized forms of the species D_R and D_O. The values of the apparent diffusion coefficients indicate the partitioning

of 1,2-naphthoquinone-4-sodium sulfonate between oil droplet, surfactant film and aqueous domain.

The rotating disk voltammograms of 1,2-naphthoquinone-4-sodium sulfonate displayed single reduction wave in pure aqueous and in micelles and microemulsion media. Except, in C_{18}DMB micelle it displayed two waves. It was found that on increasing the rotation speed there is a negative shift (~20 mV) in the half-wave potential ($E_{1/2}$) indicating the chemical reversibility. Logarithmic analysis of the rotating disk voltammograms were performed for testing the thermodynamic reversibility. The plots of i_l versus $\omega^{1/2}$ in all media showed linear correlations passing through the origin. This behaviour indicates that the reduction process takes place under mass transfer control. The slopes of these plots were used to determine the apparent diffusion coefficients in various media.

The chronocoulometry technique was used to estimate the amount of adsorbed 1,2-naphthoquinone-4-sodium sulfonate on the electrode surface in micellar solutions and microemulsion systems. Values of the amount of adsorbed reactant species were found to be in the order of 10^{-9} mole/cm^2.