REVIEWS

Electron transfer redox reactions in the micellar and liquid crystalline media

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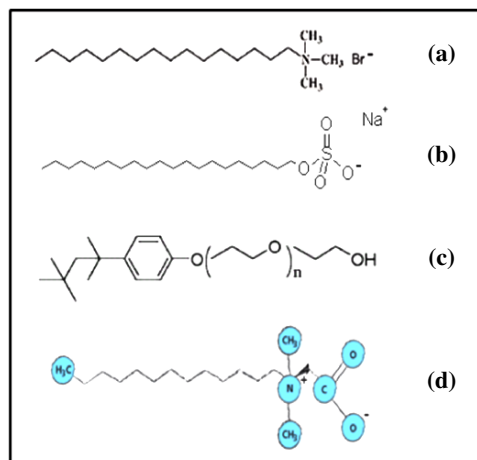
Abstract | The lyotropic liquid crystalline phases are formed by the aggregation of surfactant based micelles in the aqueous or other solvent media. They are of fundamental interest as many of the lyotropic liquid crystalline phases resemble the biological environment. An excellent example comes from the many surfactants that can form the lamellar phase in the aqueous medium such as bilayers, which are very much akin to lamellar phases formed by the lipids in the living systems. Due to this special property of the lyotropic liquid crystalline phases, they may be explored to study many of the complex processes occurring in the biological media. Among them, electron transfer reactions play a major role as they influence many of the biological processes including the nerve communications. There are several reports of the redox reactions in the micellar as well as liquid crystalline phases. In the liquid crystalline phase, most of the studies have been reported in the cubic or lamellar phase. The present review describes some of the redox reactions studied in the micellar as well as in the lyotropic liquid crystalline phases. We have focused especially on the shift of the redox potentials and the diffusion of the redox probes in the micelles and liquid crystalline phases.

1. Introduction

Surface active agents or the surfactants are molecules that have a hydrophilic head group and a hydrophobic tail group. The head group may be either a cationic, anionic, neutral or even a zwitter-ionic. For example, while cetyl trimethylammonium bromide (CTAB) is a cationic surfactant, sodium dodecyl sulfate (SDS) is an anionic surfactant. Polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether popularly known as Triton X-100 is a non-ionic surfactant where the polyethoxy chain act as the hydrophilic part. Alkyl betains are popular zwitterionic surfactants. The tail group of the surfactants is made up typically of hydrophobic alkyl or other hydrocarbon chains. The structures of different type of surfactants are shown in figure 1. In a dilute solution, these surfactants behave like a simple salt solution, while at higher concentrations of the surfactants they interact together and deviate far from the properties of salt solution. The intermolecular interactions arising either due to the electrostatic or polar-polar interactions lead to the aggregation of surfactants. Above a particular concentration, known as the critical micellar concentration (cmc), they form the micelles. The cmc depends on the nature of surfactant as well as the solvent. The micelles may be defined as small aggregates of surfactants in a solution having uniform size and shape. The shape of the micelles again depends on the nature of the molecules involved. Spherical and cylindrical micelles are the most common micelles formed by surfactants. These micelles may aggregate further at higher concentrations of the surfactants, leading

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to a 2D network of the micelles to form the liquid crystalline phase. Nematic, smectic, lamellar, cubic and columnar hexagonal phases are some of the examples of liquid crystalline phases formed by the surfactant molecules in the aqueous medium.[1,2]

1.1. *Liquid crystalline phases*
Liquid crystals may be defined as the state of matter that has the properties between crystalline phase and liquid phase. They have the orientational order of crystalline phase with the dynamics of liquid phase. The different liquid crystalline phases formed by these surfactants include smectic, nematic, cubic, lamellar and columnar phases. A general discussion on these phases may be found elsewhere.[3] Among all these, the nematic phases are the simplest by considering their degree of ordering. They are mainly formed by the rod-like molecules and in the

Figure 2: Schematic representations of columnar hexagonal liquid crystalline phases.

nematic phase, these molecules have an orientation order. The average direction of orientation is denoted by a director. They have no positional order in the nematic phase. Smectic phases are closer to nematic order, with additional positional order perpendicular to the director. The bicontinuous cubic phases are the first type of lyotropic liquid crystalline phases, and were reported in the 1960's. Compared to all other liquid crystalline phases, they possess complex structures with different lattices.[3] The lamellar phases are very common in the living systems, where the lipids form the bilayer structure in the biological environment. The columnar hexagonal phases are formed by the aggregation of cylindrical micelles. A schematic representation of columnar hexagonal phase is given in the figure 2.

2. Characterization of liquid crystalline phases
Polarizing optical microscopy provides the easiest way of analyzing the liquid crystalline phases. The method is based on the birefringence formed by the liquid crystalline phases where each phase has characteristic textures associated with them. One exception to this is the cubic phase, where they have been shown to be optically isotropic in nature. A typical texture obtained for the columnar hexagonal phase is shown in figure 3. Detailed information on the liquid crystalline phases may be obtained by the small angle X-ray scattering. By the SAXS studies, the exact structure of liquid crystalline phase and the corresponding point group can be obtained. The ratio of the peaks of the scattering vector is characteristic of the different phase and can be used for the identification of the phase. For example, the columnar hexagonal phase has the characteristic peaks that are in the ratio of $1:\sqrt{3}:2$ as shown in figure 3. The NMR has also been used for the characterization of these intermediate phases.[3,4]

3. Electrochemical studies
Electrochemical studies provide an easy assessment of the properties of the electrolytic medium. Techniques like cyclic voltammetry and electrochemical impedance spectroscopy may be used as a primary tool for this purpose. Cyclic voltammetry (CV) can provide preliminary information about nature of the phase. For example, CV in the presence of redox probes like ferrocene has been used for the measurement of self-diffusion coefficient of micelles in aqueous media.[5] The approximation used in their study was that each micelle contain one molecule of the redox probe, thereby the measurement of the diffusion coefficient of ferrocene gives the self-diffusion coefficient of the micelle. Such studies can provide information about the micellar structure as well as the interaction between redox probes and the surfactants in the medium as describes in the following sections.
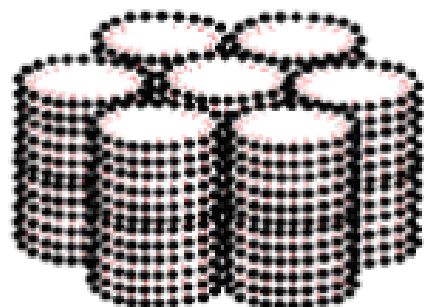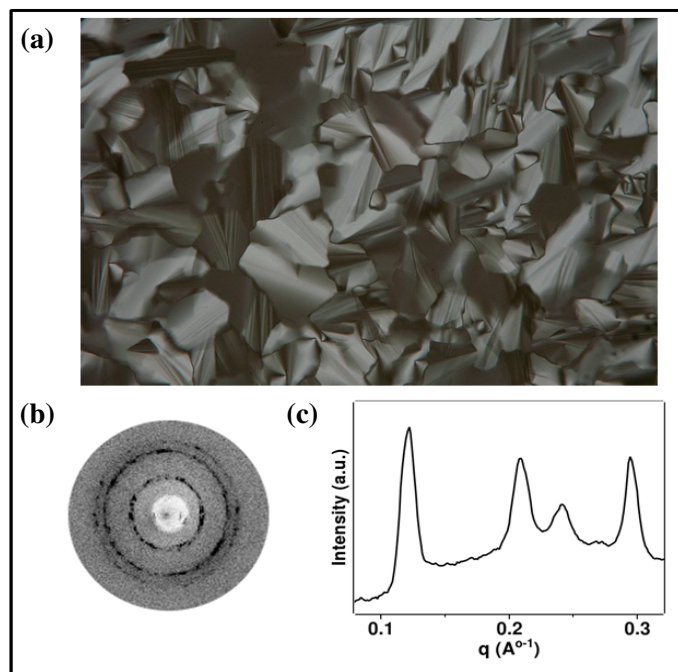
Figure 3: (a) Polarizing optical micrograph of columnar hexagonal phase (b) Small angle X-ray diffraction pattern of the columnar phase and (c) scattering vector vs. intensity plot for columnar phase of Triton X-100/water system.

(a)

(b)   **(c)**

3.1. Cyclic voltammetry in the micellar medium

Electron transfer reactions in the micellar systems have been studied extensively by several groups. Lee et al. have studied the effect of surfactants on the reduction potential of viologen in micelles and showed that the formal potential of viologen redox reaction varies with the nature of the surfactant used.[6] In their work, viologen was found to have the highest redox potential in the micelles of Triton X-100, a non-ionic surfactant, followed by cationic and anionic surfactant micelles, respectively. This behavior has been explained in terms of the stability of the ions in the micelles. Chen et al. have studied the redox reaction of ferrocene in a nitrobenzene-water emulsion.[7] Kostela et al. have reported the redox reaction of a viologen derivative, N-tetradecyl-N′-methyviologen (TMV) in a variety of surfactants. They have shown that the half-peak potential vary depends upon the charge of the surfactant. The $E_{1/2}$ value was lowest in a negatively charged micelle while the value was observed to be very high in the non-ionic micellar medium.[8] Molina et al. have demonstrated that electrochemical studies provides a method for revealing the behavior of redox probes in the reverse micelles of AOT/water system using ferrocyanide as a redox probe. They have discussed about the potential shift in the reverse

micelle that originate from the structure of the probe in the presence of surfactant.[9] Rusling et al. have carried out a series of electrochemical experiments in the micellar medium. They have used different redox probes like ferrocene, bromophenyls, bipiridyl derivatives, etc in the micellar medium.[10–14] They have also demonstrated that the electro-catalytic effects of molecules vary in the micellar media formed by different surfactants.[14–18]

3.2. CV in liquid crystalline media

As mentioned before, the lyotropic liquid crystalline phases are formed by the aggregation of micelles at higher concentration of the surfactants. Since the constituent components in the lyotropic liquid crystalline phases are same as that of the micelles, a close similarity can be expected in the qualitative properties of the redox probes in the micellar as well as in the liquid crystalline phases. This is due to the similar kind of interactions between the surfactant molecules and the redox probes and is reflected in the half-peak potentials shifts of the redox probes in the micellar and liquid crystalline phases when both the phases are formed by same surfactant. On the other hand, the orientation of the redox probes may vary depends upon the nature of the liquid crystalline phase formed. For example, the nature of the orientation of redox probes within the hydrophilic or hydrophobic parts of the liquid crystal medium has large implications in the nature and rate of diffusion of the probes. As a result, the diffusion coefficient of the probes depends more on the nature of the liquid crystalline phase than that of the surfactant that forms the phase.

Bilewicz and co-workers have prepared a series of electrochemical sensors using lyotropic liquid crystalline cubic phase modified catalytically active electrodes.[19–22] Ropers et al. have used a cubic phase for the immobilization of cholesterol oxidase on electrodes, where the cubic phase was prepared from either monoolein or fluorinated ethoxylated alcohol. They have demonstrated that the cubic phase offers a good medium for the immobilization of enzymes and offers a possibility for biosensor applications.[20] Rowinski et al. have studied the electrochemical properties of hydrophilic redox probes, viz., ferrocenecarboxylic acid and $[Ru(NH_3)_6]^{3+}$ in a bicontinuous lipidic cubic phase, and found that the diffusion of these species in the hydrophilic channels is more efficient than in the widely used nafion membrane, a proton-conducting perfluorosulfonate gel.[21–22] Razumas et al. have studied the redox reactions of several probes in cubic phases.[23–24] They have demonstrated that these cubic phases can be used for the redox behavior of biologically important compounds

also.[25–28] Kostela *et al.* have studied diffusion and electron-transfer properties of a variety of redox systems in a bicontinuous cubic phase and in a lamellar phase of monoolein and amphiphilic viologen derivatives using cyclic voltammetry and chronocoulometry.[8,29–30] They have reported a significant decrease in the diffusion coefficient values in the cubic phase. Compared to other liquid crystalline phases, the columnar hexagonal phase (H1 phase) has not been explored much for the redox reactions. Columnar hexagonal phase of Triton X-100/water system is a simple system as far as the preparation is concerned.[31] Recently we have studied the electrochemical properties of several redox probes in the columnar hexagonal phase of Triton X-100/water system. Our focus was mainly on the half-peak potential shift of the redox reaction as well as the diffusion coefficient of the redox probes in solvent and liquid crystalline media.[32–33]

3.3. Half-peak potential shift of the redox probe

One of the general observations in all the electrochemical studies of redox probes in the presence of surfactants is that the oxidation and reduction potentials shift in the micellar and liquid crystalline media vis-à-vis the aqueous medium. The shifts have generally been attributed due to the interaction between the redox probe and the surfactant, especially the electrostatic interactions, as described below. A representative CV is shown in figure 4, where it is clear that the redox potentials shift in the LC phase compared to the aqueous phase.

Figure 4: Cyclic voltammogram of 1mM 4-benzoquinone+1mM 4-hydroquinone/0.1M NaF in (a) aqueous phase and (b) columnar liquid crystalline phase at a scan rate of 20mV/s on a gold disc electrode using Saturated Calomel Electrode as the reference electrode.
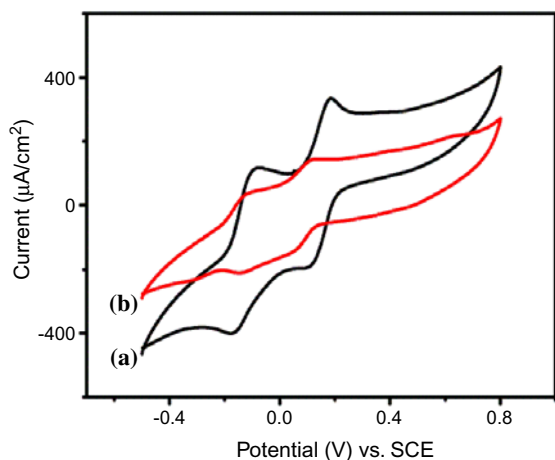
3.3.1. Ferrocyanide/ferricyanide reaction

The redox reaction of the ferrocyanide/ferricyanide is one of the most studied process in the micellar and LC phases. It has been observed that the redox potential shifts to a lower value in the presence of surfactants (from 164 mV in the aqueous solution to about 100 mV in columnar phase, potential vs. saturated calomel electrode, SCE). The main reason for this shift has been due to the hydration of the redox ions in the surfactant systems. In the micellar state of CTAB/ hexadecane/1-butanol /water, for example, the shift has been attributed to the hydrogen-bonding effects between the probes cyano groups and the water molecules associated with the micelle.[34] Since in the micellar state, most of the water molecules are bound with the surfactant to form the micelle, it is expected that the total solvation sphere of the redox probe to be less in the micelle compared to the aqueous medium. Moreover the stability of the ions in the micellar media also contributes to the redox potentials of the probes. On the contrary, in the AOT reverse micellar state, the half-peak potential was observed to be shifted to higher potentials, which is also a function of the AOT concentration.[9] The authors have attributed this to the association of the counter ions (K^+ ions) with the probe. They have shown that as the association increases, the $E_{1/2}$ shifts to more positive value. In the presence of non-ionic surfactant, the potential was shifted to a lower value which has been attributed to the better stability of the less-charged, oxidized species in presence of the non-ionic surfactant.[32]

3.3.2. Hexaammineruthenium system

This system is somewhat less studied in the micellar and liquid crystalline media. In a liquid crystalline phase of the non-ionic surfactant, Triton X-100/water system, we have observed that the $E_{1/2}$ value does not vary much compared to the aqueous phase ($E_{1/2}$ around—170 mV and variation of about 20mV). It is well-known that this system undergoes an outer sphere electron transfer reaction at the electrode/electrolyte interface. Moreover both the oxidized and reduced species are cationic species. Since the reaction undergoes outer-sphere redox reaction, the redox potentials is independent of the environment of the redox reaction that occurs.[32]

3.3.3. Quinone redox reaction

The quinone redox reaction is comparatively complex due to the involvement of protons in the redox reactions. It is well-known that the redox reaction of quinone is reversible only in the presence of H^+ ions. Recently Quan *et al* have shown that in an un-buffered solution, different species like

Q^{2-}, Q^{-}, Qh^{-} and Qh_2 may exist which depends on the pH of the solution.[35] It has been observed that in the CV, the peak potentials depend on the medium. This is mainly due to two reasons; the electrostatic interaction between the redox species and the medium on the one hand, and the formation of hydrogen bonding with the solvent molecules or the surfactants on the other hand. The mechanism of the redox probes in non-aqueous solutions in the presence of proton donors have been studied previously.[36] The solvent effect on the redox reaction was also studied in the literature in different organic solvents.[37–38] It has been shown that in an organic medium, the potential of the redox reaction of benzoquinone may be tuned by the addition of different concentration of benzoic acid, which can act as a proton donor.[39] On the other hand, the effect of substitution on the aromatic ring in the redox reaction in organic media has been studied by Bauscher et al.[40] Recently, in the cubic system, it has been observed that the redox process is quasi-reversible.[22] This probably may be attributed to the absence of H^+ ions, which is necessary for the redox reaction. We have also observed a similar behavior in the columnar hexagonal phase of Triton X-100/water system.[33] The stability of the redox species in the medium as well as its hydrogen bonding network that forms with the solvent molecules contributes to the half-peak potential shifts. For example, in the H1 phase described above, the $E_{1/2}$ has shifted to a lower potential (150 mV in the aqueous phase to about 87mV in the columnar phase) due to two reasons namely (a) the less ionic species, quinone is more stabilized in the presence of non-ionic surfactant of Triton X-100 and (b) the availability of the hydrogen bonding with the water molecules. Since in the present case, the reaction is in the absence of excess protons, Q^{2-} and Qh^- species are expected to be the main species than Qh_2, the hydrogen bonding is more favored with the quinone molecules than the reduced species which therefore leads to the oxidation at lower potentials.

3.3.4. Viologen system

Viologen species are one of the most studied redox probes in the micellar and liquid crystalline media as compared to other redox probes mainly due to the possibility of amphiphilic nature of the substituted viologen molecules. A general trend in the redox behavior in the viologen is that the first reduction is highly reversible compared to the second reduction. This may probably attributed to the lower solubility of the MV^0 species compared to the mono and di cationic species. As a result, most of the studies have been concentrated on the first reduction-oxidation of the species. This

particular peak again highly depends on the nature of surfactant used. It has been shown that the $E_{1/2}$ is at the lowest potential in the presence of an anionic surfactant, and shifts to a more positive potential in the presence of cationic surfactant (-0.66 V in anionic, around -0.53 V in cationic and -0.5 V in non-ionic surfactants, using Ag/AgCl reference electrode).[8] Interestingly, the half-peak potential is highest in the case of non-ionic surfactant than in the presence of cationic surfactants. These results have been attributed to the stability of the viologen species due to electrostatic interaction between with the surfactant molecules. Almost similar behavior is observed in the micelles as well as in different liquid crystalline media.[6,8,29,30,33]

3.3.5. Ferrocene and its derivatives

Compared to all other redox systems, the ferrocene – ferrocenium has been the most studied probe in the micellar medium. This is due to the fact that the reduced species, ferrocene is highly hydrophobic, while the oxidized species, ferrocenium is highly hydrophilic in nature. Because of this, the ferrocene molecules occupy the inner core of the normal micelles, whereas after oxidation, they tend to come out of the core.[41] The main consequence of this is the high energy cost of oxidation and thereby the positive potential shift of ferrocene and other ferrocene derivatives in cationic as well as non-ionic micelles (from about 0.142 V in the solvent to about 0.275 V in the columnar phase). In the presence of anionic micelles, due to the better electrostatic interaction of ferrocenium with the negatively charged surfactant, the redox potential is observed to shift to a lower value.[7,32,33]

3.3.6. Other redox systems

Electrochemical redox behavior of several aryl halides have also been studied in the micellar media.[10–18] It has been observed that the redox behavior enhances in the presence of surfactant, due to the better solubility of the probes in media. The Half-peak potentials of aromatic halides like bromophenyls are shown to be a function of the surfactant as well as probe concentration.

3.4. Electrochemical impedance spectroscopy (EIS)

EIS may be employed in the study of redox reactions as a more quantitative method for getting parameters like the kinetics of redox reaction and diffusion coefficient of the redox probe. It is performed normally at the formal potential or the half-peak potential, as the case may be, of the redox reaction. This assumes that the concentration of both oxidized species and the reduced species to be the same at the half-peak

Figure 5: The real and imaginary components of the impedance for 1 mM benzoquinone/1 mM hydroquinone system in (a) aqueous phase and (b) columnar hexagonal liquid crystalline phase at their corresponding half-peak potentials for the first reduction-oxidation process.
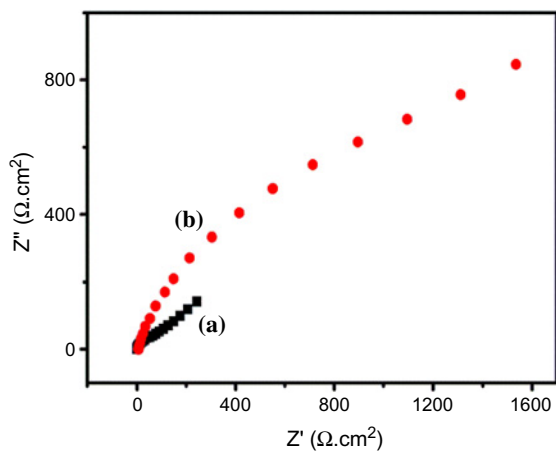
potential. An ac voltage of small perturbation (about 10 mV) is applied and the response of the system (impedance) is measured at different frequencies. A plot of the real and imaginary components of the impedance of diffusion controlled reaction is represented in figure 5. The response is then modeled as a combination of electronic components like resistance, capacitance etc. A typical diffusion controlled reaction can be modeled as a combination like Randle's circuit as shown in the figure 6, where R_u is the solution resistance (uncompensated resistance), C_{dl} is the double layer capacitance, R_{ct} is the charge-transfer resistance that related to the kinetics of the reaction and Z_w is the Warburg impedance which is related to the diffusion of the redox probes in the medium. The diffusion coefficient of the probe can be calculated using the following equations.[42]

$$Z_W = (2/\omega)^{1/2} \cdot \sigma \tag{1}$$

$$\sigma = (RT/2^{1/2}n^2F^2D^{1/2}A)(1/C_o + 1/C_R) \tag{2}$$

where ω is the angular frequency, R and T has usual meanings, n is the number of electrons involved in the redox reaction, F is Faraday constant, D is the diffusion coefficient of the probe, A is the area of the electrode, C_O and C_R are the concentration of oxidized and reduced species in the solution.

3.4.1. *Diffusion coefficient of the probes*

The diffusion coefficient values of the redox probes in the micellar and liquid crystalline phases are generally lower compared to normal solvent medium. The extent of decrease depends on the nature of the redox probe as well as that of the micelle or liquid crystalline phase.

In a liquid crystalline medium, the diffusion of the redox probe is found to depend on the nature of the probe as well as the structure of the medium. The hydrophilic probes have higher diffusion coefficient than the hydrophobic probes in the liquid crystalline phase. For the hydrophilic probes like $[Fe(CN)_6]^{3-/4-}$ and $[Ru(NH_3)_6]^{2+/3+}$ the diffusion coefficient in the liquid crystalline phase is observed to be around an order of magnitude less than that in the aqueous medium. For the $[Fe(CN)_6]^{3-/4-}$ system, it has reduced to about 3×10^{-6} cm^2/s in the columnar phase from the value of 2×10^{-5} cm^2/s in the aqueous phase. In the $[Ru(NH_3)_6]^{2+/3+}$ system, the values are 1.2×10^{-5} cm^2/s in aqueous medium and 6.8×10^{-7} cm^2/s in the columnar phase. A lower diffusion of the probes is expected due to the more viscous nature of the LC medium. In this respect a similar behavior is observed in the columnar hexagonal phase as well as in the cubic phase. Interestingly, methyl viologen with lower alkyl chain substitutions show a very high diffusion coefficient in the LC phase that may probably due to the linear shape of the molecule. With longer alkyl chain substituted viologen molecules, the diffusion coefficient is very less due to the amphiphilic nature of the molecule. The quinone system shows much more complex behavior due to the possibility of formation of hydrogen bonding with the solvent or the surfactant

Figure 6: A simple Randle's equivalent circuit model for fitting the electrochemical impedance spectroscopic data for diffusion controlled redox reaction.
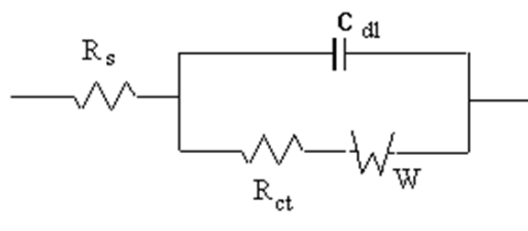
molecules. Moreover for the quinone and ferrocene systems, the redox reactions involve changes in the nature of the species from hydrophilic to hydrophobic or *vice versa,* as explained previously. Inside the micelles, the diffusion of the hydrophobic probes is expected to be very less due to the interaction of alkyl chains of the surfactant with the redox probes. Outside the micelles, diffusion of the hydrophilic probes will be comparatively facile through the un-hindered water channels, unless any hydrogen bonding is present. For the ferrocene systems, in a columnar hexagonal phase, the diffusion coefficient is observed to decrease by nearly 2 orders of magnitude, due to the following two reasons, (1) the ferrocene is present inside the micelle and (2) specific interaction of ferrocenium ions with the polyethoxy chains of the surfactant (Triton X-100) and the charge-transfer complex formation. The diffusion coefficient of ferrocene has decreased from about 6×10^{-6} cm^2/s to about 8×10^{-8} cm^2/s, while for the quinone system the values are 3×10^{-6} cm^2/s and 8.6×10^{-8} cm^2/s in the columnar phase.[8,22,29,30,32,33]

The liquid crystalline phases have been widely used for the biological experiments. Cubic phases have been shown to be an ideal medium for the immobilization of enzymes and proteins on the electrode surfaces and biosensor applications. The lyotropic systems have also been modeled for the drug delivery in biological media. The lyotropic systems have the advantage in such studies with their higher capability of dissolving both hydrophilic as well as hydrophobic molecules simultaneously.[43,44]

4. Conclusion

One of the major approximations involved in the electrochemical studies in the presence of surfactant is that the effective area of the electrode remains same in both aqueous as well as in the surfactant-based media. This of course assumes that the adsorption of the surfactant which blocks the effective electrode area has not been factored in the analysis. Since the adsorption of molecules especially the surfactants, depends upon the surface charge on the electrode, it is difficult to separate out the adsorption part. In cyclic voltammetry, the surface adsorption varies as a function of the potential and therefore with time. This will affect the orientation and local concentration of the redox probes near the electrode surface. Nevertheless, in the lyotropic columnar phase, it has been shown by us that the assumption of planar diffusion of the probes is valid and the set of equations defining it in aqueous phase can be employed for the characterization in liquid crystalline phases. The studies described here also demonstrate that the redox potentials of the

probes in the presence of surfactants is decided by the nature of the probe and the surfactant used. From the diffusion coefficient values obtained in these studies in the liquid crystalline phases, we also infer that the diffusion of hydrophilic probes is not hindered in the LC phases to the same extent as hydrophobic probes. This is owing to the restricted movement of the hydrophobic redox species through the inner core of the micelles. We believe that these studies are very important in providing important information on such processes as targeted drug delivery in living systems and the immobilization of enzymes and other bio-molecules on the electrode surfaces for sensor applications.

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