

Beneficial role of surfactants in electrochemistry and in the modification of electrodes

R. Vittal^{a,*}, H. Gomathi^b, Kang-Jin Kim^a

^a Division of Chemistry and Molecular Engineering, and CRM-KOSEF, Korea University, Seoul 136-701, South Korea

^b Central Electrochemical Research Institute, Karaikudi-630 006, India

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Abstract

This review deals with the beneficial use of surfactants in various fields of electrochemistry, in general and in the modification of electrodes with immobilized electroactive species, in particular. Special emphasis is laid on the modification of electrodes with metal hexacyanoferrates (MHCs). After an introduction and brief notes on fundamentals of surfactants, and their applications in electrochemistry, covering some of the very important works in the past two decades involving beneficial use of surfactants, the article gives a brief account on metal hexacyanoferrate modified electrodes and the salient features of our published results on the beneficial role of cetyltrimethylammonium bromide (CTAB), a cationic surfactant, in the modification of electrodes with MHCs and their derivatized oxides, and with titanium dioxide.

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Keywords: Surfactants; Modified electrodes; Micelles; CTAB; Metal hexacyanoferrates

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* Corresponding author. Tel.: +82 2 3290 3542; fax: +82 2 3290 3121.

E-mail address: javittal@yahoo.com (R. Vittal).

1. Introduction

Being surface active, surfactants naturally have a very large impact on chemistry of current interest. Their role in electrochemistry is well documented in the past few decades [1–4]. A surface active agent (surfactant) is one which tends to accumulate at a surface or interface. A prerequisite for surfactants to be surface active is the property of these molecules to adsorb at the interface between bulk phases, such as air and water, oil and water or electrode and solution. The distinct structural feature of a surfactant is the hydrophilic region of the molecule or the polar head group which may be positive, negative, neutral or zwitterionic and the hydrophobic region or the tail that consists of one or more hydrocarbon chains, usually with 6–22 carbon atoms. Thus they are also called amphiphiles, i.e., compounds having both polar and nonpolar regions in their molecules. Depending on the chemical structure of the hydrophilic moiety bound to the hydrophobic portion, the surfactant may be classified as cationic, anionic, nonionic or zwitterionic.

Two important properties of surfactants viz., adsorption at interface and aggregation into supramolecular structures are advantageously used in electrochemistry. Surfactants are able to modify and control the properties of electrode surfaces. The use of surfactant structures to alter or enhance reaction rates has been known for decades [5]. More recently, surfactant structures have been used to control reaction pathways. Research on the influence of surface active agents on the kinetics of electron transfer reactions at electrodes spans half a century [1,3,4,6–11]. There was evidence as early as in the 1950s that surfactants could be used to control electrochemical reactions and solubilize organic compounds for electrochemical studies in water. A large fraction of the research in controlling electrochemical reactions with surfactants as well as aggregate characterization by electrochemical methods has been published within the past 20 years. They are found to control the electrochemical catalysis through their microstructures. Research since the late 1970s has demonstrated that coulombic and hydrophobic interactions with surfactants can stabilize various electrochemically produced ion radicals [12]. Much early work was done on mercury electrodes, especially on dropping mercury electrodes (DME). Until recently, few studies trying to directly elucidate the supramolecular structures of surfactant adsorbate films were made. A good part of the research on the influence of adsorbates on heterogeneous electron transfer rates addressed the problem in terms of inhibition of electron transfer and electrostatic interactions. More recent work concerning surfactants adsorbed from micellar solutions has focused on elucidating, or utilizing, aggregate structures formed on the electrode. Surfactant molecules generally adsorb at the interface between two bulk phases such as air and water, oil and water or electrode and solution as pointed out earlier. Adsorption of surfactants on electrodes can have a profound influence on electrochemistry in fluids.

In principle, if structures, dimensions, and polarities of interfacial aggregates and the positions of electroactive centers within them are known, the effects on electrochemical kinetics can be predicted by using modern theories of electron transfer [13]. Such predictions would take into account the influence of distance on electron transfer and the environment surrounding the reactants [14]. It is quite possible that the dynamics of the surfactant aggregates also plays a role.

Surfactants find, in general, several applications, e.g., in textile industry, cosmetics, pharmaceutical, household, laundering and general cleaning uses, in the preparation of paints, lacquers, inks and pigments, in leather technology, in petroleum and lubricant and paper industries, in photography, printing and graphic arts and in the manufacture of rubber and resins [15,16]. Surfactants have a wide range of applications as emulsifiers and dispersants. Miscellaneous and specific uses of surface active agents are well described in literature [15–17]. J.H. Fendler and E.J. Fendler have exhaustively described the catalysis of organic reactions in micellar and macromolecular systems [5]. Solubilization of organic compounds in surfactant aggregates is a well known phenomenon, especially in electrochemistry. Surfactants such as gelatin and Triton X-100 began to be used routinely in electroanalytical chemistry to suppress the so-called streaming maxima at DME, shortly after the invention of polarography by Heyrovsky in 1922 [3]. Early landmark papers featuring effects of surfactants also appeared in the literature of organic electrochemistry.

From the large size of literature available on chemically modified electrodes, it is clear that surface modification is an important area of study in modern electrochemistry and any research carried out in this direction will be of interest, especially due to the several application possibilities of these electrodes. Introduction of surfactants in this area of work adds a new and useful dimension to these investigations. It is well founded that very few investigations were made on the role of surfactants in surface modification of electrodes, as can be seen from the meager publications available in this regard, considering the fact that research has been carried out on surfactants in electrochemistry for more than six to seven decades. No particular class of materials has been studied well until now for modification process in the presence of surfactants. We are the first group to study the influence of surfactants on the modification of electrodes with metal hexacyanoferrates (Fe/Ni/Co-HCF) [18–20] and with NiHCF/CoHCF-derivatized oxides [21]. We could not find any report on their influence on the modification of electrodes with metal hexacyanoferrates. Xun et al. have published an extension of our work on the modification of electrode with cobalt hexacyanoferrate using CTAB, in which they have studied the electrocatalytic behavior of the electrode towards the oxidation of dopamine [22].

In this contribution we will review the significance of surfactants in electrochemistry, with specific emphasis on their influence on the modification of electrodes with different coating materials, especially with metal hexacyanoferrates.

The paper also incorporates the salient features of our works on the beneficial influence of CTAB in the modification of electrodes with iron/nickel/cobalt–metal hexacyanoferrates, with their derivatized oxides, and also with TiO₂.

2. Micelles

Having mentioned about the properties adsorption and aggregation of surfactants, it is necessary to have knowledge about micelles. The term micelles refers to aggregates of surfactants. They are formed from soluble surfactants above a critical micelle concentration (CMC). They possess regions of hydrophilic and hydrophobic character. At very low concentrations surfactants do not associate themselves to form micelles. In water the polar charged head groups face the water and the hydrocarbon chains face the interior of the micelles. Reverse micelles are associations of surfactant molecules containing a water core, formed in an organic phase by the addition of surfactants.

2.1. Critical micelle concentration

The narrow range of concentration at which the micelles first become detectable is the CMC of the amphiphile. CMC also refers to that concentration where abrupt changes or sharp discontinuity in physical properties such as conductivity and surface tension occur. The CMC is very characteristic for each surfactant, where dynamic aggregates are formed and it is necessary to know the CMC value for the commonly employed surfactants for quantitative understanding of experimental data. CMC values for commonly used surfactants range from 10^{-4} to 10^{-2} M [17,23].

2.2. Structures of micelles

Just above the CMC, micellar structure is considered to be roughly spherical or cylindrical [5,23]. A simple schematic representation of such structures is given in Fig. 1. However, the exact structure of micelles is still somewhat controversial. Although an oversimplification, Fig. 1 is a useful model for

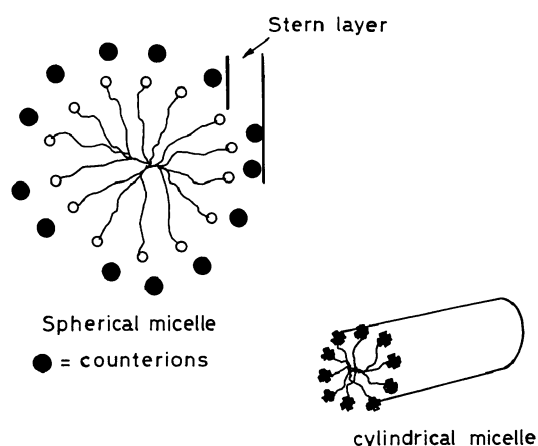


Fig. 1. Spherical and cylindrical micelles. Circles are head groups or counterions; wiggly lines are hydrocarbon tails.

qualitative understanding of experimental results. Hydrophobic cores of micelles have diameters of 10–30 Å.

2.3. Aggregation number

The number of monomers in a micelle, the aggregation number (N) determines the size and geometry of the micelle and hence is an important quantity. Aggregation numbers for surfactants in aqueous solution generally range between 10 and 100.

2.4. Stern layer

The outer ionic surface in a micelle, which also contains associated waters of hydration, is called the stern layer. Many of these ions in the stern layer are bound to their counter ions. 60 to 90% of the ionic surface is neutralized by these counter ions in aqueous surfactant solutions without added salt [23].

2.5. Gouy–Chapman region

Surrounding the stern layer exists the Gouy–Chapman region which contains both counter ions and oriented water molecules.

3. Traube's rule

In 1987, Isidor Traube, a German physical chemist reported that the surfactant concentration, needed to give a specific value of interfacial tension at the air–water interface, decreased three-fold for each additional methylene group in the chain. Such regular changes in surfactants with increasing chain length follow what has become known as Traube's rule. It describes the regular changes in surface activity with increasing chain length. The knowledge about Traube's rule becomes important to understand the differences in electrochemical properties brought forth by surfactants of different chain lengths.

4. Adsorption of surfactants at solid–liquid interface

In general, adsorption begins well below the CMC of the surfactant, as evidenced, for example by the low concentrations of Triton X-100, a nonionic surfactant (0.001–0.005%), which are employed for maximum suppression in polarography. Results above and just below the CMC for ionic surfactants on Pt and Hg electrodes [11,24–27] are in agreement with formation of bilayers or hemimicelles (surface micelles). Furthermore, multilayers of surfactants formed in solutions at concentrations well above the CMC, especially at extreme potentials of opposite sign of that of the surfactant head group, are suggested by voltammetry of hydrophobic probes [28,29]. On the other hand, studies with some electroactive surfactants seem to suggest that saturation coverage corresponds to a monolayer [30–34].

Conventionally, adsorption studies involve the determination of adsorption isotherms, zeta potentials, particle wettabil-

ity, and heats of adsorption. It is interesting to note that only in the past decade most of the phenomenon on adsorption of surfactants at solid–liquid interface is understood. Adsorption isotherms for isomerically pure anionic surfactants were measured on alumina and kaolinite from aqueous solutions by Scamehorn et al., who presented a model that incorporated bilayer adsorption, lateral interactions, and two dimensional phase transitions below CMC of the surfactants and “hemimicelle” formation beyond a certain concentration [35]. Chandar et al. made fluorescence probe studies on the structure of the adsorbed layer of dodecyl sulfate at the alumina–water interface and gave a molecular model that is in agreement with the concept of hemimicellization of surfactants at the interface [36]. Yeskie and Harwell have extended the concept of hemimicelles to admicells on mineral oxide surfaces, and explained their formation depending on different conditions [37]. Gao et al. proposed two steps of adsorption on silica gel; in the first step surfactants are adsorbed through interactions with solid surface and in the second step they are adsorbed through interactions among the adsorbed surfactants, in which “surface micelles” are formed, which are spherical in shape [38]. From the results obtained for adsorption isotherms, flotation, ESR, and fluorescence, Fan et al. [39] concluded that the adsorption mechanism for alkyltrimethylammonium bromides on negatively charged alumina is in accord with the four region model, which was originally based on the model proposed by Somasundaram et al. in describing the adsorption of anionic surfactant on positively charged alumina [40]. The first direct visualization of surfactant hemimicelles by atomic force microscopy (AFM) of the electrical double layer was made by Manne et al. [41]. Sharma et al. have characterized adsorbed cationic surfactants on mica substrate by an AFM study and illustrated their different morphologies, depending on their concentrations [42]. Singh et al. have used FT-IR/ATR-techniques coupled with contact angle, adsorption, and zeta potential techniques to investigate the structural transitions taking place as the concentration of the surfactant is increased, and found that initially surfactants adsorb randomly and individually, and then above a certain critical concentration they form hemimicelles and, as the concentration is further increased, randomly oriented spherical aggregates, under their experimental conditions [43]. Schulz and Warr have studied the structure of adsorbed layers of sodium dodecyl sulfate (SDS) and tetradecyltrimethylammonium bromide (TTAM) on titanium dioxide (rutile) and kaolinite, and of TTAB and CTAB on quartz, imaged by AFM above their respective CMCs, and shown that all these surfactants form globular surface micelles on these substrates, but under very different conditions [44]. Li and Tripp have used infrared spectroscopy to identify the aggregated structures of adsorbed CTAB on negatively charged TiO_2 surfaces and shown that even at very low concentrations (10^{-7} to 10^{-6} M), small aggregated CTAB structures adsorb through electrostatic interaction with negative sites on the surface, which gives way to hemimicellar and, possibly, admicelle structures at higher CTAB concentrations; above the CMC micellar structures adsorb on the surface [45].

5. Specific application of surfactants in electrochemistry

5.1. Electroplating

Surfactants are generally used in electroplating to clean metal surfaces and also to accelerate hydrogen evolution at the cathode. Fatty alcohol eoxylates and sulphates are often used, and in some cases also alkyl benzene sulfonates [46]. Fluorosurfactants are particularly advantageous in electroplating due to their chemical stability.

Surface active agents are also used in electroplating aiming at the following beneficial effects [47]:

- widening of the operating range with respect to pH, temperature and current density,
- modification of the crystal size of the deposited metal, so that the brightness of the resulting plate improves,
- reduction of the surface tension of the electroplating solution. Due to this, detachment of gas bubbles from the cathode is facilitated and pitting and pinholing are avoided, and
- cleaning of the metal surface as a preparatory step to plating, e.g., in nickel plating baths. Best deposits are obtained here at the lowest surface tension, which is brought forth by the addition of surface active agents.

Uchida and co-workers have patented an invention which relates to a non-cyanide based Au–Sn alloy plating bath comprising a solution of gold salt, a solution of tin salt etc., wherein the polymeric cationic surfactant or agent is contained for enhancing the luster and reflow properties [48]. In plating silver, gold and copper from alkaline solution of the double cyanides, surfactants shorten or eliminate the buffing operation (grinding a surface to remove extrusions or to expose underlying metal), which is otherwise required to produce a bright polished surface [47]. Surfactants influence the depolarization of an electroplated coating and the efficiency of plating operations. The effects of surfactants include changing the polarization potentials at the cathode [49] and altering the smoothness of the plate, the grain size, rate of grain growth and adhesion of the grains to the substrate and to each other [50]. Metallic nickel was electrodeposited from aqueous nickel(II) acetate dissolved in the liquid crystalline templating mixture Brij 56 and Brij 78, and the electrochemically accessible surface area of this film has been estimated to be 100 times greater than samples grown without a templating electrolyte [51]. Yoshida et al. have developed a new electroplating technology using nonionic surfactants to prepare high quality nickel films with higher uniformity, smaller grain size (sub-100 nm) and higher Vickers hardness, compared to those of the films obtained by conventional electroplating method without using surfactant [52]. Brij 56, a nonionic surfactant, or pluronic P123, a triblock copolymer, also a surfactant, was used to template the electrodeposition of mesoporous nickel films onto foamed nickel electrodes; the method was found to produce a 30- to 35-fold increase in surface area of the three-dimensional electrodes, which is

beneficial for various applications including electrochemical detectors, batteries, and fuel cells [53].

5.2. Corrosion

Cationic micelles of long-chain quaternary ammonium bromides (e.g. CTAB) are reported to act as inhibitors of corrosion of steel, and the inhibitory effect of the surfactants increases with alkyl chain length at concentrations above their CMC [54]. Atia and Saleh have reported that the cationic surfactant cetylpyridinium chloride (CPC) showed high inhibition efficiency for the corrosion of low carbon steel in 1 M H_2SO_4 and that protection efficiencies of up to 97% were measured [55]. El Achouri et al. have synthesized gemini surfactants of the type 1,2-ethanediyl bis-(dimethylalkylammonium bromide) and studied their inhibitive effect on the corrosion of iron in hydrochloric acid, and concluded that these compounds are good inhibitors of iron corrosion and reach their maximum inhibition efficiency near their CMC [56]. Adding surfactants to acidic media is often the only efficient and rather cheap method of rust protection of metals. The general mechanism of corrosion inhibitors lies in the fact that they form an adsorbed film on the metal to be protected [57]. Liu et al. have shown that undoped polyaniline-4-dodecyl-phenol complex (PANI-DDPH) is an effective corrosion inhibitor, and that the surfactant improves the wet adhesion property between the coating and the metal surface [58].

5.3. Batteries and fuel cells

Xingyun et al. have described in an article about the improvement of performance of a Zn/Ni battery due to the addition of salts and surfactants to the electrolyte. The utilization of $\text{Ni}(\text{OH})_2$ electrode reached 70–80%. The loss of average capacity was limited to 0.2–0.5% per day and consequently the shelf life of the battery was prolonged [59]. Hiroshi et al. in their patent [60] described a secondary Ni/ H_2 battery with improved alkaline electrolyte, which contained anionic surfactants. The battery showed low self discharge. Use of surfactants to suppress self discharge of a lead–acid battery with paste type electrodes was also claimed by Karohiro et al. in a patent [61]. Jin and co-workers had invented a lithium ion battery using a nonaqueous electrolyte, comprising of a fluorine-based nonionic surfactant that was substituted with various functional groups at the end group, and claimed high capacity and excellent charge/discharge properties for the battery [62]. Wang et al. have used the surfactant, dodecyl-dimethyl(3-sulfo-propyl)ammonium hydroxide (SB12) for the synthesis of carbon supported Pt and Pt/Ru electrocatalysts for polymer electrolyte fuel cells, to prevent the metal colloids from aggregation during the reduction process without influencing the deposition of the colloids onto the carbon support [63].

5.4. Electrometallurgy

Surface active substances are most widely used in electrochemical industry. Use of surface active substances in

electrocrystallization process makes it possible to obtain metal precipitates with pre-assigned properties, increased current efficiency and precious metal content in the slime [64].

5.5. Electrocatalysis

A nano- Al_2O_3 modified glassy carbon (GC) electrode was reported to have shown a great enhancement to the oxidation of estradiol, when adequate concentration of CTAB was added into the sample solution [65]. Dang et al. have demonstrated that the cationic surfactant, CTAB on the surface of an acetylene black electrode could significantly decrease the overpotential of dioxygen reduction, and increase the reduction peak current of oxygen [66]. Fu et al. [67] have achieved a new kind of multilayer of didodecylmethylammonium bromide (DDAB) and 1:12 phosphomolybdic anions (PMO_{12}) on the surface of wax-impregnated graphite (WIG) electrode by ion exchange and electrostatic interaction, which has exhibited an excellent electrocatalytic activity toward the reduction of BrO_3^- anion in 0.5 M H_2SO_4 and has many advantages, such as simple fabrication, fast response, good stability, notwithstanding the basic electrode size and topology. Choi et al. have developed a new method to prepare thin mesoporous platinum films utilizing potential-controlled surfactant (SDS)-assembly, and demonstrated their enhanced electrocatalytic properties towards methanol oxidation, compared to those of non-porous platinum films [68]. CTAB–clay-modified glassy carbon electrode confined with ferrocenedicarboxylic acid was found to determine ascorbic acid in the presence of uric acid, and showed good anti-fouling properties towards surface active materials [69]. Electrochemically stable fullerene (C_{70}) modified electrode was made from cationic surfactant DDAB using glassy carbon electrode; electron transfer rates were enhanced for the redox couples of C_{70} due to the presence of the surfactant on the electrode, which was also proved to be applicable for the electrocatalysis of hemoglobin in aqueous solution [70]. Shaofang Lu has prepared a novel multiwall carbon nanotubes (MWNTs)-modified GC electrode in the presence of a surfactant, dihexadecyl hydrogen phosphate, and used for the electrochemical determination of tannins with advantages of high sensitivity, rapid response, excellent reproducibility, and extreme simplicity [71]. Instead of MWNTs, Chunhai Yang used singlewall carbon nanotubes (SWNTs) for the modification and found similar advantages for the termination of tinidazole [72].

5.6. Electroanalysis

Triton X-100 was used in voltammetry to give good wetting properties to the graphite electrode [73]. Clelland et al. have described in a patent [74] the use of surfactants in preparing ion selective electrodes for use in mixed solvent systems. These electrodes can be used with ionic surfactants and are relatively inexpensive. They will operate over a wide range of homologs exhibiting little differential selectivity, and offer a good Nernstian calibration with up to 20% v/v EtOH (aq.) or 10% v/v HCl present. Hu et al. have reported a rapid and sensitive

linear sweep polarographic method for the determination of progesterone based on a 40-fold higher sensitivity for its determination, because of synergistic adsorption of progesterone and CTAB on the electrode surface [75]. High performance liquid chromatography (HPLC) having an electrochemical (EC) detector electrode of pyrolytic graphite coated with a film of ionomer Naflon and the water-insoluble surfactant didodecyl-dimethylammonium bromide (DDAB) was used to achieve separation and detection of all six bromo- and chloro-acetic acids [76]; this method also detected tribromoacetic acid, which has not been determined simultaneously with other halogenated acids by reported chromatographic methods. Zhang et al. have developed an electroanalytical method for the voltammetric determination of diethylstilbestrol (DES) at a carbon paste electrode using the surfactant cetylpyridine bromide and phosphate buffer as the medium, utilizing the fact that the oxidation peak currents of DES increase significantly in the presence of the surfactant, compared with those in the absence of it [77]. Wen et al. have demonstrated that dopamine can be determined in the presence of 100 times excess of ascorbic acid, by separating their overlapping anodic peaks in the presence of CTAB micelles; the same authors have also shown that quantitative determination of the two compounds can be made in the presence of each other using SDS micelles, as in its presence the anodic peak current of dopamine enhances greatly [78]. Yi et al. have described a new voltammetric method for the determination of phenol using a Naflon-modified glassy carbon electrode in phosphate buffer (pH 8) in the presence of CTAB, and have shown that phenol has a very sensitive oxidation peak at 0.47 V (vs. SCE) [79]. Wei et al. have described a method for the determination of glycyrrhizic acid (GA) based on the fact that polarographic current of GA enhanced doubly by both CTAB and dissolved oxygen [80].

5.7. Electroorganic chemistry

Micellar catalysis is a well established phenomenon in the electrochemical production of organic compounds. Franklin and co-authors [81,82] elucidated the role of cationic surfactants added in the oxidation of inorganic anions to increase the yield of the product at a platinum electrode. The same author with co-worker Iwunze showed that many organic compounds not oxidizable on platinum electrodes in 0.2 M NaOH give

voltammetric waves in micellar solutions of Hyamine/NaOH [83]. They also used Pt coated with hyamine (a surfactant) to enhance the rate of hydrolysis of ethyl benzoate [84]. Rauniyar and Thomalla have studied anodic cyanation of aromatic substrates in cationic, anionic and nonionic micellar systems [85]. Electrohydrodimerizations of activated olefins are of considerable commercial importance, an example being dimerization of adiponitrile in the commercial production of its hydrodimer adiponitrile. High concentrations of tetraethylammonium *p*-toluene-sulfonate (a surfactant) facilitated higher yields of the dimer [86]. Chen and co-workers have achieved direct reduction of oxyhemoglobin on a bare glassy carbon electrode and proved that the reduction reaction is promoted by the cationic surfactant hexadecyltrimethylammonium bromide when it is added in the electrolyte solution [87]. Hovestad et al. have reported that electrochemical codeposition of zinc-polystyrene composite was enhanced when a cationic surfactant, cetylpyridinium chloride was added to the electrolyte, owing to the prevention of aggregation of polystyrene particles by the surfactant [88]. Poly (3,4-ethylenedioxythiophene) was synthesized from aqueous solution by anodic oxidation of its monomer by adding anionic surfactants; use of surfactants enabled very stable and highly conductive polymer, increased solubility of the monomer and deposition current, and decreased oxidation potential [89]. Qingfeng et al. have used CTAB to increase the reaction rate for the electrochemical production of benzaldehyde from toluene in an undivided cell in the presence of the couple V^{5+}/V^{4+} , and obtained a maximum current efficiency of 156.3% under the conditions of 11 M H_2SO_4 , 2.7×10^{-4} M CTAB, current density 1.25 mA cm^{-2} and 0.0128 M V^{5+} [90].

5.8. Photoelectrochemistry

Dixit et al. have reported a significant enhancement of power output from a totally illuminated thin-layer (TITL) photogalvanic cell, consisting of a synthesized surfactant thionine ($C_{10}ThH^+$, I) and Fe^{2+}/Fe^{3+} couple in an anionic microemulsion medium, compared to that obtained in a cationic microemulsion medium and in water [91]. Groenen et al. have shown that addition of Triton X-100 micelles to the aqueous acidic cell solution of a ferrous/thionine photogalvanic cell leads to an improvement in efficiency of the cell by a factor

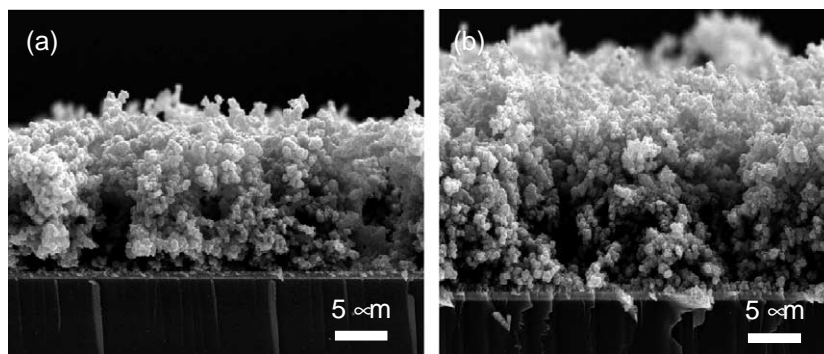


Fig. 2. Cross-sectional view of FE-SEM images of electrodeposited and annealed TiO_2 films, prepared from $TiCl_4$: (a) without and (b) with CTAB.

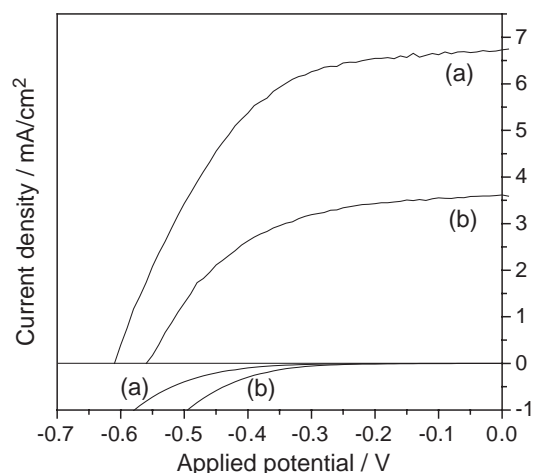


Fig. 3. J - V curves under illumination (upper two curves) and in the dark (lower two traces) of DSSCs prepared from hydrolyzed TiCl_4 ; (a) with and (b) without CTAB.

of 5, relative to that of the cell free of micelles [92]. Sharmila et al. have constructed a phenosafranin-EDTA photoelectrochemical cell with CTAB, which showed a 50-fold increase in the solar energy efficiency, as well as an increased storage capacity, compared to those of a cell without surfactant [93]. We have developed a new strategy involving the introduction of CTAB for the cathodic deposition of TiO_2 from hydrolyzed TiCl_4 and TiCl_3 solutions by cyclic voltammetry [94] and obtained crack-free and non-transparent anatase TiO_2 films on conducting glass. CTAB increased the film thickness (Fig. 2) and reduced the deposition period, compared to those of a case without it. The CTAB-promoted film led to an increased energy conversion efficiency of the corresponding dye-sensitized solar cell (DSSC), compared to that obtained in the case of a cell made without surfactant. Similar enhancement of conversion efficiency (Fig. 3) is observed by us in the case of a DSSC with TiO_2 film electrode, which was prepared by simple precipitation of TiO_2 in the presence of CTAB [95].

6. Modified electrodes in micellar solutions

The electrochemistry of redox active substances in micelles has been reviewed in the recent past [96,97]. Excellent progress has been made with polymers [62,98]. Kuwabata et al. have demonstrated the utility of coating the electrode substrates with a mixture of polystyrene, an ionic surface active agent and an ionic electroactive species such as $\text{Ru}(\text{bpy})_3^{2+}$ or $\text{Fe}(\text{CN})_6^{3-}$ [99]. Simultaneous formation of separate layers of conducting polypyrrole and insulating Al_2O_3 on aluminum electrode by electrolysis, using an anionic surfactant electrolyte (*n*-dodecylbenzenesulfonate) was reported by Naoi et al; a test electrolytic capacitor formed in this way displayed an excellent impedance-frequency characteristic, superior to that of a conventional electrolytic capacitor [100] (a mechanism involving advantageous utilization of the amphiphilic nature of the surfactant was proposed by the authors). Octadecylsilyl-coated electro-

des were studied in the hope that they would coadsorb surfactant and electroactive reactants from micellar solutions [101]. An analyses of these electrode surfaces by X-ray photoelectron spectroscopy (XPS) showed that moderate washing with water removed the surfactant, but not the ODS-coatings. However, micellar solutions provided moderate control over heterogeneous electron transfer rates at ODS-electrodes. For surfactant and electroactive ions of the same charge sign, the electron transfer rate was partly inhibited. Ferrocene and ions of charge opposite to the surfactant showed faster rates [101]. Conductive polyaniline (PANI) was prepared in one step in water-dispersed medium in the presence of the nonionic surfactants, NP40 (nonylphenolethoxylate) or surfamide; it was reported that the first surfactant insures the medium stability and the second one enhances the conductivity by the occurrence of H-bond with the PANI backbone [102]. Poly(3-methoxythiophene) films were electrosynthesized on Pt electrodes by oxidation of 3-methoxythiophene in aqueous micellar media, using anionic, cationic and nonionic surfactants, thanks to the decrease in oxidation potential of the thiophene by the surfactants, which otherwise is higher than that of water and thus a drawback for the electropolymerization [103]. Electrode passivation caused by electrochemical oxidation of phenol was reported to be dramatically reduced by using a poly(3,4-ethylenedioxythiophene)-poly(sodium-4-styrenesulphonate) composite electrode (the second compound in the composite being a surfactant) [104]. Electropolymerization of ethylenedioxythiophene in micellar solutions displayed an enhanced rate, as compared to that obtained in submicellar solutions or surfactant-free solutions; micellar surfactants were also found to shift the oxidation potential to less positive values [105]—a beneficial effect in terms of saving the energy. Microtubules of polypyrrole were synthesized by an electrochemical template-free method in the presence of the surfactant β -naphthalenesulfonic acid (β -NSA) as a dopant, in which the absorbed micelles of the surfactant were proposed to act as templates in forming ppy-NSA tubules [106].

Electrodes coated with clay films have also been examined in surfactant solutions. Natural clays are layered aluminosilicate cation exchangers. They adsorb cation surfactants, which form bilayer or hemimicelle coatings on the clay surface. Surfactant treated clay colloids can coadsorb nonpolar reactants [107,108]. Clay-modified electrodes (CMEs) were made by depositing colloidal Na bentonite (ca. 500 nm thickness) on pyrolytic graphite (PG). Tris(2,2'-bipyridyl) cobalt (II) dication was taken up by the CMEs in the absence and presence of CTAB micelles [109]. It gave separate CV reduction peaks for Co(II) at -1.2 V and Co(I) at -1.5 V. Films of tetraalkylammonium surfactant bilayers, intercalated between colloidal clay layers, were prepared by Okahata and Shimizu [110] as membranes with controlled permeability. Hu and Rustling [111] have reported electrochemical properties and examples of electrochemical catalysis in films made from clay colloids and dialkyldimethylammonium surfactants. Brahimi et al. [112] have demonstrated that the formation of the cationic surfactant bilayer confers anion-exchange properties to the clay and found

that redox anions such as ferricyanide $[\text{Fe}(\text{CN})_6]^{3-}$ can be concentrated into a cetyltrimethylammonium+clay-modified electrode (CTA⁺+CME). In addition they showed that neutral redox active reagents, such as ferrocene, can also be incorporated. Incorporation of anionic species in CTAB-coated clay-modified electrodes and their electrochemical behavior are recently reported by Falaras and Petridis [113]. A CTAB/carbon paste electrode developed by Hu et al. has shown an exchange current (i_0) of 6.79×10^{-5} A, while the value with the corresponding bare carbon paste electrode was 2.72×10^{-7} A; this electrode was applied in a novel approach for the preparation of DNA modified electrode [114], and has additionally showed enhancement effect in thyroxine reduction [115]. Khodari et al. and Kauffmann et al. have reported that the modification of carbon paste electrodes with naturally occurring amphiphiles (phospholipids, fatty acids) showed marked biomembrane interactions [116,117]. Digua et al. have proved that the modification of a carbon paste electrode by the surfactant hexadecyl sulfonic acid (sodium salt) enabled strong cation exchange properties of the modifier and increased electron transfer rate [118,119]. Shi and co-workers [120] found that by combining the cationic didodecyldimethylammonium with $[\text{Ir}(\text{OEP})]_2$ on a graphite electrode surface, the stability and the electrocatalytic activity of the iridium porphyrin have increased significantly. Using this tactic they were able to fashion electrode surfaces at which the four-electron reduction of O_2 to H_2O proceeded at unprecedented positive potentials that exceeded even those obtained at platinum electrodes.

7. Role of surfactants in the modification of electrodes with metal hexacyanoferrates and their derivatized oxides

In the design of chemically modified electrodes efforts are made [121–124] for stable immobilization of certain molecules on an electrode surface, so that the electrode thereafter displays the chemical, electrochemical, optical and other properties of the immobilized molecules. The study of modified electrode surfaces has had a profound effect on research in the field of electrochemistry in the last three decades [118,125–131]. There has been an ever increasing interest in electrodes coated with thin polymeric films containing redox active centers [126,132,133]. Various inorganic materials such as clays [134], zeolites [135], transition metal oxides [136,137], transition metal particles [138], and polyoxometallates [139] have been used to fabricate chemically modified electrodes. Recently carbon nanotubes are used as modifying agents of electrodes for various applications, such as capacitors, catalysis, sensors etc. [140–142]. Most of the research focused on organic polymers as modifying agents. Recently inorganic polynuclear microstructures have been a subject of increasing activity as well [143–150]. Among these latter materials transition metal hexacyanoferrates have received particular attention owing to their interesting electrical and electrochemical properties [151–160]. A large volume of literature on the permanent modification of substrate electrodes with substances containing easily oxidizable/reducible groups has been reviewed by Murray

[126]. Jyh-Myng Zen et al. have updated recent developments in chemically modified electrodes (CMEs) towards analytical applications with 179 references, mentioning various chemically modified electrodes, analytes, preparation procedures etc. [161].

Electrodeposition of transition metal hexacyanoferrate films has been carried out by several groups worldwide [162–177]. Modified electrodes of Ni and Co oxides through derivatization of corresponding NiHCF or CoHCF coated conducting electrodes were reported earlier by our group of researchers [178,179]. Such oxide-modified electrodes have been shown to be good electrocatalysts [180] and also found to be useful for amperometric sensing [181]. Additionally the above oxide electrodes have been explored for their electrochromic properties and reported earlier [182,183]. There is considerable interest at the present time in the development of non-emissive display devices based on the electrochromic behavior of hydrated metal oxides [184–186]. The two novel materials, viz., cobalt hexacyanoferrate and cobalt oxide are proposed as counter electrode coatings on ITO that can be used along with electrochromic working electrodes [179]. Sheela et al. [180] have reported the results of the catalysis of nickel oxide, obtained through surface derivatization of NiHCF on a GC electrode, on electrooxidation of alcohols and sugars, known to be not easily oxidizable.

We have carried out research in our laboratories in which transition metal hexacyanoferrates, namely Prussian blue and its analogues, and the derivatized oxides of nickel and cobalt hexacyanoferrates, were used along with surfactants as

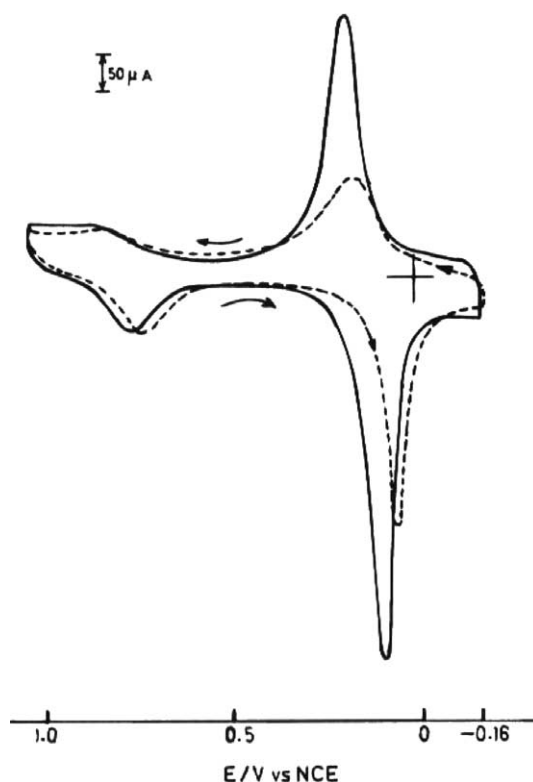


Fig. 4. CV response of PB (dashed line) and PB+CTAB (solid line) modified electrodes in 0.1 M KCl at 0.1 V s^{-1} .

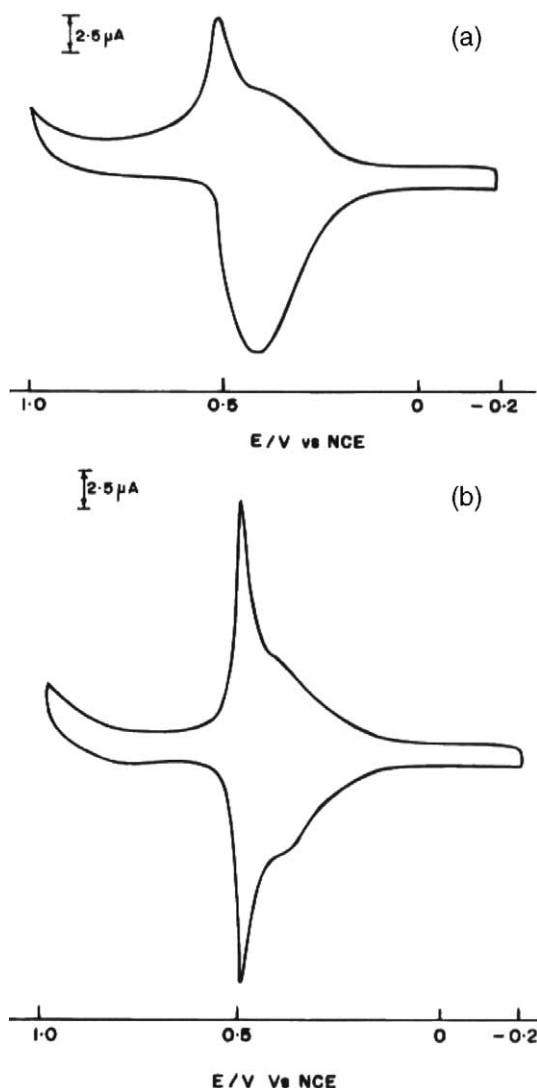


Fig. 5. (a) CV response of a NiHCF modified GC electrode in 0.1 M KCl at 0.1 $V s^{-1}$. (b) CV response of a NiHCF+CTAB modified GC electrode in 0.1 M KCl at 0.1 $V s^{-1}$. Potential scan from -0.2 to 1 V.

modifying agents on electrodes. Investigations of this type have not been reported until now and should prove to be useful not only from basic understanding point of view but from their possible applications in electroanalysis [187–192], electrocatalysis [11,180,193,194], electrochromism [195–198], batteries [199–201], fuel cells [202,203], electrochemical capacitors [204,205], solar cells [206,207], electrolytic production [208], corrosion-resistance [209] etc.

Experiments were conducted using three types of surfactants, viz. cetyltrimethylammonium bromide (CTAB, a cationic surfactant), sodium lauryl sulphate (SLA, an anionic surfactant) and Triton X-100 (a nonionic surfactant). Encouraged by the excellent beneficial effects of CTAB in the modification of electrodes with PB film, detailed investigations were carried out on PB and some of its analogues, to assess the comparative performance of these films prepared in the presence and absence of CTAB. Ni and Co hexacyanoferrate films, formed both in the presence and absence of CTAB were further

modified into their corresponding oxide films and the related beneficial influences of CTAB were studied.

The experimental details are as follows: a three electrode cell assembly with platinum counter electrode, normal calomel reference electrode (NCE), and glassy carbon/platinum working electrode (0.03 and 1 cm^2 , respectively) was used. All cyclic voltammetric experiments were carried out with a potentiostat coupled to a voltage scan generator and an x–y recorder.

In all preparative solutions for forming the metal hexacyanoferrate films, 0.1 M KCl was used as electrolyte, 0.5 mM FeCl_3 /0.5 mM NiCl_2 /0.5 mM CoCl_2 solutions were used to prepare the corresponding iron, nickel and cobalt hexacyanoferrate films. In each case 0.5 mM $\text{K}_3\text{Fe}(\text{CN})_6$ was added consequently. CTAB of 0.92 mM, which corresponds to the critical micelle concentration, was added wherever required (in case of SLA and Triton X-100 they were used at their CMCs). The modification with the film was achieved by cycling the electrode potential between -0.2 and 1 V at 0.1 V/s for 15 min. Oxides of Ni/Co were derivatized from their corresponding hexacyanoferrates by cycling the potential of these already modified electrodes in 0.1 M NaOH at 100 mV/s and 50 mV/s, respectively. Response of metal hexacyanoferrate modified electrodes was observed in 0.1 M KCl at a scan rate 0.1 $V s^{-1}$ (in case of CoHCF 0.1 M HCl was added to the electrolyte).

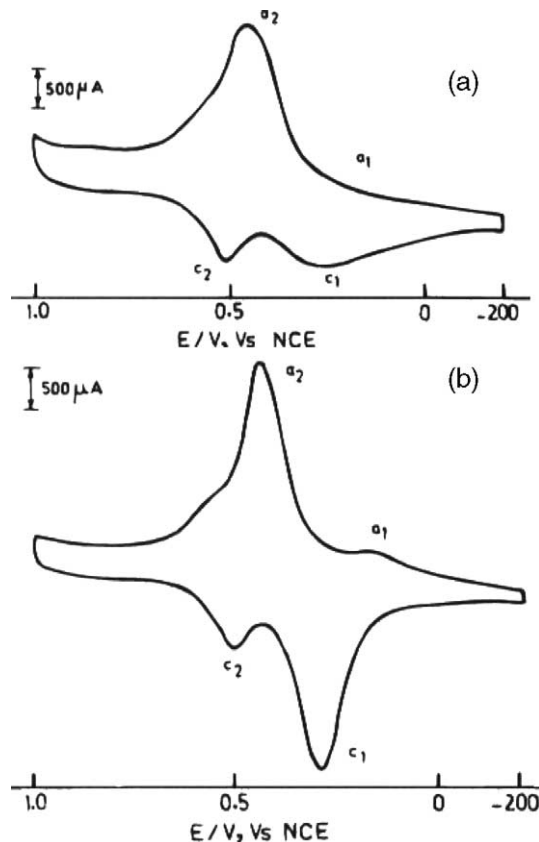


Fig. 6. (a) CV response of a CoHCF-modified electrode in 0.1 M KCl+0.1 M HCl at 0.1 $V s^{-1}$. (b) CV response of a CoHCF+CTAB-modified electrode in 0.1 M KCl+0.1 M HCl at 0.1 $V s^{-1}$ (a1, c1 are set of anodic and cathodic peaks at less positive potentials and a2, c2 are set of anodic and cathodic peaks at more positive potentials). Potential scan from -0.2 to 1 V.

Responses for Ni and Co oxide electrodes were obtained in the same 0.1 M NaOH used for obtaining the oxides. Absorbance spectra were obtained using a Hitachi U-3400, UV–vis–near infrared spectrophotometer.

We present here essentials of our results published already in detail [18–21]:

- Both anionic (SLS) and nonionic (Triton X-100) surfactants behaved similarly in suppressing the performance of the PB modified electrode [18].
- The beneficial influence of CTAB is restricted at its critical micelle concentration (0.92 mM). Use of still higher concentrations (say ≈ 2 mM) resulted in poor modifications, as evidenced by negligible PB activity in the modified film [18].
- Films of all the three hexacyanoferrates (Fe, Ni and Co), when prepared with CTAB, showed great improvements in their CV responses in terms of yields of large peak currents (Figs. 4, 5 and 6) and enhancement of reversibility. The films formed in the presence of CTAB are thicker and more stable, compared to those films formed

in the absence of CTAB [18–20]. A striking symmetry of anodic and cathodic voltammograms is observed in the case of NiHCF film formed in the presence of CTAB, compared to that in the absence of it (Fig. 5) [19]. CTAB showed improved resolution of the surface redox processes in case of the CoHCF film (Fig. 6) [20].

- Observation of behavior of FeHCF, NiHCF and CoHCF films (both with and without CTAB) in KCl, NaCl, LiCl and NH_4Cl showed that CTAB does not affect the normal transport characteristics of K^+ , Na^+ , Li^+ and NH_4^+ ions through the channels of the film. It is inferred that the presence of CTAB during the film formation has only catalytic effect and does not alter the chemical composition of the film [19,20].
- The beneficial effects are reflected by the respective oxide derivatives of NiHCF and CoHCF in alkaline media, as revealed by the CV responses in Figs. 7 and 8 [21].

Electrochromism can be defined as a color change in a material by an applied electric field or current. Such materials

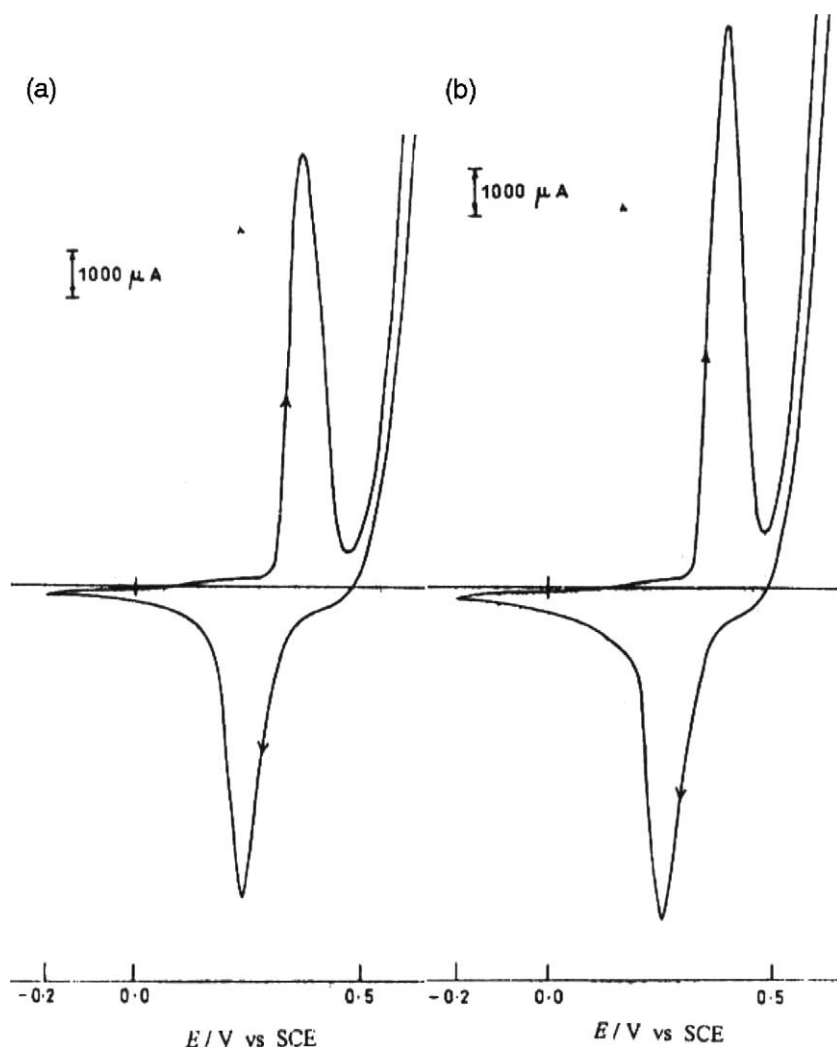


Fig. 7. (a) CV response of a NiO-modified electrode in 0.1 M NaOH at 100 mV s^{-1} . (b) CV response of a NiO+CTAB-modified electrode in 0.1 M NaOH at 100 mV s^{-1} .

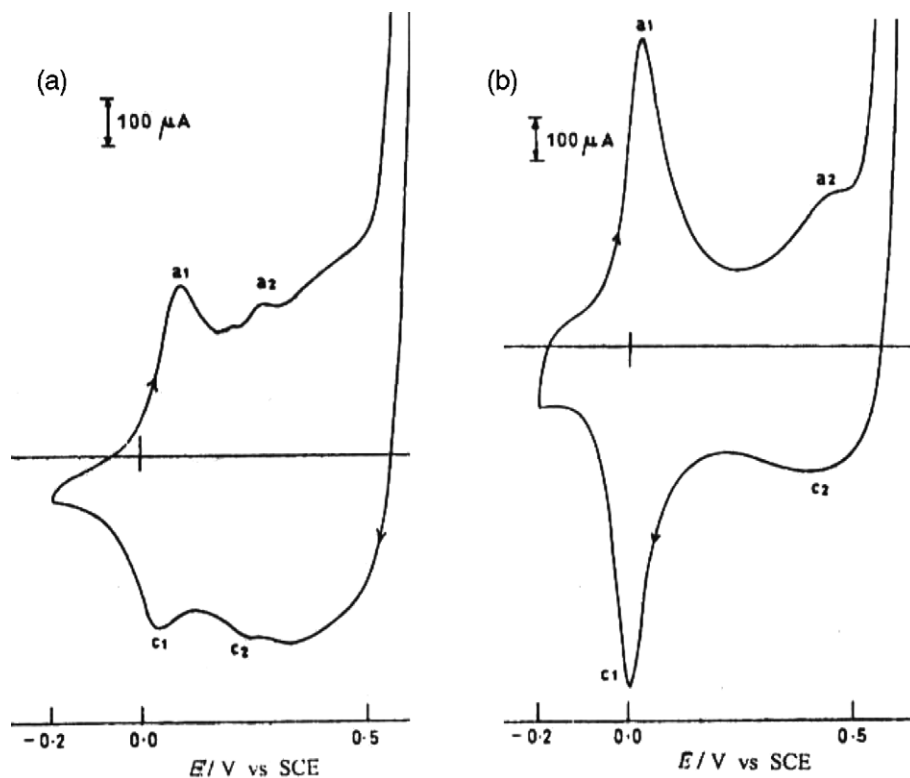


Fig. 8. (a) CV response of a CoO-modified electrode in 0.1 M NaOH at 50 mV s^{-1} . (b) CV response of a CoO+CTAB-modified electrode in 0.1 M NaOH at 50 mV s^{-1} . (a1, c1 are set of anodic and cathodic peaks at less positive potentials and a2, c2 are set of anodic and cathodic peaks at more positive potentials).

are used in display devices, sensors, cameras and smart windows. Prussian blue is one such electrochromic material. The visible absorbance spectra of PB and PB+CTAB films on platinum electrodes are shown in Fig. 9. Curve “a” represents the spectrum of PB film, while curve “b” that of PB+CTAB film. Regions of wavelength above 600 nm correspond to the blue colour of Prussian blue material. It can be seen that in the case of film with CTAB there is a steep increase in the absorbance in this region, whereas the absorbance does not show any increase in the case of the film without CTAB. The optical absorbance spectra for PB film with CTAB showed a

noticeable increase in optical density up to 35%. The enhanced color intensity in the presence of CTAB is beneficial for electrochromic devices using Prussian blue films.

8. Conclusions

The review article presents an insight into the role of surfactants in electrochemistry. Numerous references in the article indicate their variety of influences, e.g., in the catalysis of organic reactions, solubilization of organic compounds, control of electrochemical reactions, altering or enhancing of reaction rates and control of reaction pathways. An exhaustive description of their applications in practically almost all the branches of electrochemistry reflects their importance in electrochemistry.

Promotion in electroplating techniques, inhibition of corrosion, improvements in the performance of batteries and fuel cells, new or improved electroanalytical techniques are established as beneficial influences of surfactants in a survey of works on these aspects. A chronological discussion on the adsorption of surfactants at liquid–solid surfaces makes one visualize possible structures of surfactants depending on experimental conditions. A brief account of research on chemically modified electrodes and of our research on the influence of CTAB on the modification of electrodes with transition metal hexacyanoferrates and their derivatized oxides can form a basis for further research in this direction, especially owing to the applications of these electrodes in variety of fields cited in the article.

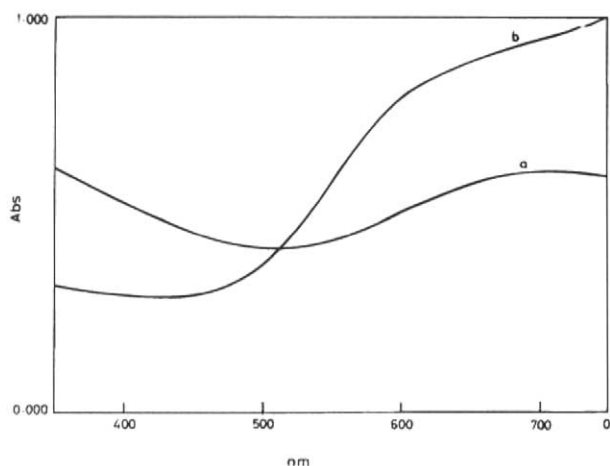


Fig. 9. Absorption spectra of (a) PB and (b) PB+CTAB films on platinum electrodes.

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