

Beneficial Effects of Cetyltrimethylammonium Bromide in the Modification of Electrodes with Cobalt Hexacyanoferrate Surface Films

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A new strategy involving the introduction of a cationic surfactant, cetyltrimethylammonium bromide (CTAB), for the modification of electrodes with cobalt hexacyanoferrate (CoHCF) film has been found to be beneficial. The surfactant has been found to influence the electrochemical properties of the CoHCF-modified electrode by way of enhancement of voltammetric currents and reversibility of redox reactions. CoHCF surface films deposited by a potential cycling procedure in the presence and absence of CTAB are compared for K^+ transport characteristics, using cyclic voltammetry (CV). CV parameters in 0.1 M KCl + 0.1 M HCl for electrodes modified both in the presence and in the absence of CTAB and diffusion coefficient values obtained from double potential step chronocoulometry at different pulse widths are presented and discussed. A comparative study is made for the transport behavior of K^+ , Na^+ , Li^+ , and NH_4^+ ions through CoHCF films, prepared both in the presence and in the absence of CTAB.

1. Introduction

In the past decade, there has been considerable interest in the preparation and characterization of electrodes modified with cobalt hexacyanoferrate (CoHCF) film,^{1–5} an analogous compound to ferric ferrocyanide (Prussian blue) reported by Itaya et al.⁶ We have reported the preparation and electrochemical characterization of a cobalt analogue of Prussian blue earlier.⁷ Reports are available from the literature on the infrared and Moss Bauer spectra,^{1,2} electrochemical impedance spectra, X-ray absorption near-edge structure (XANES), and visible spectra⁴ of cobalt hexacyanoferrate surface films on electrodes. There are other reports on the electrocatalytic activity of CoHCF-modified electrodes^{8,9} and enhanced stability and electrocatalytic activity of a ruthenium-modified cobalt hexacyanoferrate film electrode toward oxidation of hydrazine, thiosulfate, and chlorophenol.¹⁰ Cobalt hexacyanoferrate-modified electrodes have been shown to catalytically oxidize hydrogen peroxide and hydrazine.^{11,12} Electrochromic properties of cobalt hexacyanoferrates were studied by P. J. Kulesza et al.^{13,14} Cobalt hexacyanoferrate and its derivatized oxide are proposed for the first time as counter electrode coatings on an indium tin oxide (ITO) electrode that can be used along with electrochromic working electrodes of Prussian blue and nickel oxide at an appropriate cell assembly.¹⁵ The unique electrochromic properties of CoHCF films have been reported,^{13,14} which depend not only on the oxidation state of the system but also on the nature of alkali metal cations sorbed from the supporting electrolyte during reduction. It is reported that CoHCF film structure can selectively transport cations in to and out of it upon electrochemical cycling.^{7,16} Cobalt(II) hexacyanoferrate has face-centered cubic structure^{17,18} analogous to Prussian blue.

Though research has been carried out on surfactants in electrochemistry for more than 6–7 decades, few investigations

are made on their role in surface modification of electrodes, as can be seen from the meager publications available in this regard. No particular class of materials has been studied well to date for a modification process in the presence of surfactants. The new activity of introducing surfactants during the modification of electrodes with iron and nickel hexacyanoferrates originated from our laboratory^{19–21} and has been extended to further derivatization of oxides of nickel and cobalt from their respective hexacyanoferrates.²² A comparative study has been made on the role of different types of surfactants, namely, anionic, nonionic, and cationic, in the modification of electrodes with Prussian blue.^{19,20} The beneficial effects of the cationic surfactant cetyltrimethylammonium bromide (CTAB) in the modification of electrodes with nickel hexacyanoferrate films and with films of oxides of nickel and cobalt were reported.^{21,22}

In view of the fact that among analogues of Prussian blue CoHCF has unique electrochemical properties with respect to counterion accommodation and has been chosen as a model system by several authors^{4,17} to address the problems related to the insertion and lattice accommodation of counterions of various sizes, the novel concept reported in the present work to study these properties in the presence of a surface active agent will have many implications on the electrochemical, spectral, and structural aspects of the chosen compound, and the results will be interesting to physical chemists in general and electrochemists in particular.

The present study focuses attention on the electrochemical and cation transport properties of CoHCF films prepared in the presence of the cationic surfactant CTAB at its critical micelle concentration. The special effects observed for CoHCF + CTAB films in the presence of different supporting electrolyte cations are summarized and reported for the first time. The investigations assume importance owing to the promising potential applications of the CoHCF-modified electrodes in ion-sensing, electrocatalysis, and electrochromic display devices and in view of the added benefits achieved in the presence of CTAB.

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2. Experimental Section

A three-electrode cell, assembled with large area platinum counter electrode and normal calomel reference electrode, was used. A platinum working electrode of area 2 cm² was employed in all of the studies unless otherwise specified.

All cyclic voltammetric experiments were carried out with a potentiostat (Wenking model LB 75), coupled to a Wenking voltage scan generator VSG 72 and an X–Y recorder (Rikadenki-RW 201). Chronoamperometric and chronocoulometric experiments were performed using an electrochemical analyzer, BAS-100 A.

All chemical substances were of analytical grade and used without further purification. Double distilled water was used for preparing solutions. Solutions for modifying the electrodes with films of cobalt hexacyanoferrate both in the presence and in the absence of CTAB were freshly prepared each time. Prior to modification, the platinum electrodes were subjected to ultrasonic cleaning and flame treatment. All of the potentials reported are measured with respect to an SCE. The potential of the SCE is +0.24 V versus the standard hydrogen electrode (SHE).

The modification of the electrodes with CoHCF film involves potential cycling of the electrode in the modifying mixture, which contains 0.5 mM CoCl₂ + 0.5 mM K₃Fe(CN)₆ in 0.1 M KCl + 0.02 M HCl, from –0.2 to 1 V and back at the sweep rate of 0.1 V s^{–1} for 16 min (40 cycles). A total of 0.92 mM of CTAB, which corresponds to its critical micelle concentration, was added to the modifying mixture whenever required.

Before subjecting the electrode to potential cycling in a supporting electrolyte, the cell, the reference electrode, and the working electrodes were thoroughly washed with distilled water. Solutions were clear prior to the addition of CTAB, but its presence turned the solutions to turbid.

3. Results and Discussion

3.1. Influence of Surfactant (CTAB) on the Modification of Electrode with CoHCF Film. Platinum electrode was modified with cobalt hexacyanoferrate film using the procedure reported by us earlier and described under Experimental Section.⁷ The film was found to grow in thickness with each cycle, as revealed by the increasing charge under the redox peaks. No further growth is observed after 17–18 min of cycling, so the cycling time was restricted to 16 min in all cases, which corresponded to 40 cycles for a scan rate of 100 mV/s between potential limits –0.2 to 1.0 V. When the electrode is thoroughly rinsed with double distilled water and its response is observed in pure 0.1 M KCl + 0.1 M HCl, it retained its CV response as shown in Figure 1. The film formed is very stable over prolonged cycling of the potential between –0.2 and 1.0 V in 0.5 M KCl medium. In our earlier work,⁷ it has been noticed that CoHCF film coated over a wax-impregnated graphite electrode (WIGE) was stabilized when stored in a pure supporting electrolyte of 0.5 M KCl. In the present work, the CoHCF film coated over platinum electrode was checked for its stability by cycling it in 0.5 M KCl between potential limits –0.2 to 1.0 V for hundreds of cycles. The stabilizing strategy for the CoHCF film without the addition of CTAB is comparable to our earlier work⁷ and also to the subsequent work reported by Cataldi et al.¹⁰ wherein an elaborate account of the relatively poor stability of CoHCF in the absence of ruthenium addition is presented. It is also worthwhile to mention that even though the voltammetric profiles in K⁺- and Na⁺-containing supporting electrolyte are different (ref 7 and the present work) the lack of stability for repeated potential cycling is indeed the same.¹⁰

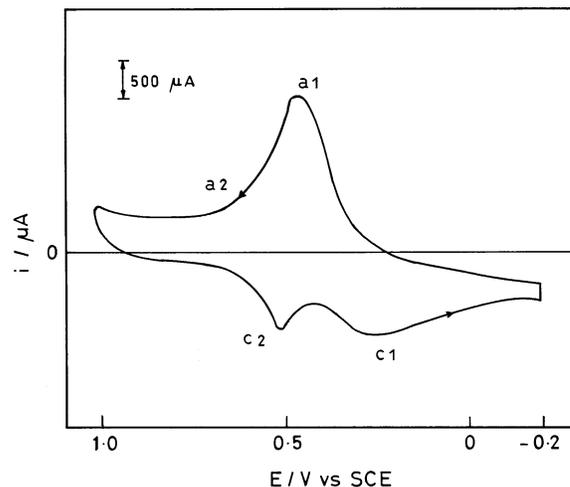
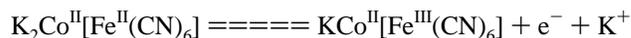


Figure 1. CV response of a CoHCF-modified electrode in 0.1 M KCl + 0.1 M HCl at 0.1 V s^{–1}.

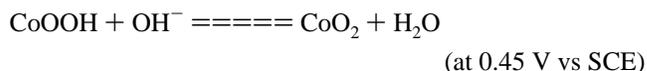
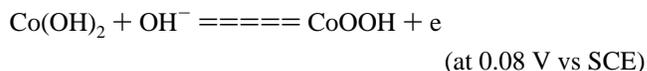
At the experimental conditions, only one broad peak (a₁) appears on the anodic side at about 0.45 V, and on the cathodic side, one sharp peak (c₂) appears at ~0.5 V and one broad peak (c₁) at ~0.3 V. In conformity with our earlier observations,^{12–14} it is noticed that two peaks (a₁ and a₂) have merged into one broad peak on the anodic side under our experimental conditions.

The following general equation may be proposed to describe redox processes of cobalt hexacyanoferrate in the film:¹⁴



The two redox peaks in KCl with CoHCF film may be accounted for by the existence of two stable forms, probably K₂Co^{II}[Fe(CN)₆] and KCo_{1.5}[Fe^{II}(CN)₆],²³ which are electroactive at different potentials.

In an earlier publication,⁷ we have indicated the possibility of oxidation of Co(II) to Co(III) in CoHCF film. Moreover, a proof for the presence of two redox states can be very well understood from the response curves of further derivatization of CoHCF film in alkali, which manifests two sets of distinct redox peaks at ~0.08 and ~0.45 V. These two redox peaks are not well resolved in KCl medium. The two sets of redox peaks in alkali medium are represented as follows.¹⁵



The two sets of redox peaks correspond to Co^{II}/Co^{III} and Co^{III}/Co^{IV} redox states of cobalt as reported earlier. The treatment with alkali has a templating action on the CoHCF film and brings to focus the ordered structure²² of oxide species onto the surface, which also stands as a solid test to offer information on the probable stoichiometric composition, under carefully controlled experimental conditions, and structural changes associated with the CoHCF film in alkaline medium.

The observation on the beneficial role played by the cationic surfactant CTAB (cetyltrimethylammonium bromide) in the modification of electrodes with PB and NiHCF films^{20,21,24,25} served as a driving force to attempt the modification of electrode with CoHCF film in the presence of CTAB. As reported in our earlier studies,²⁰ the concentration of CTAB corresponds to its

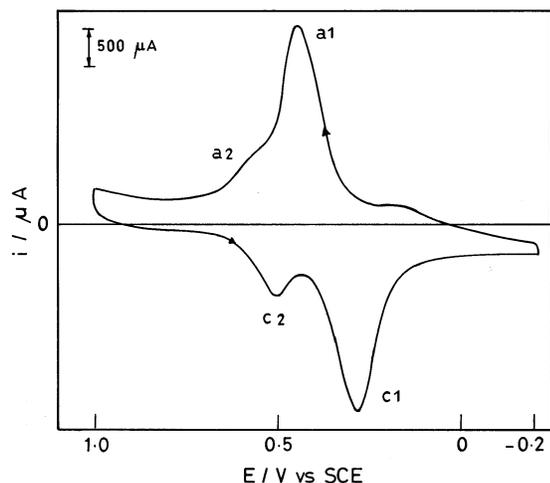


Figure 2. CV response of a CoHCF + CTAB-modified electrode in 0.1 M KCl + 0.1 M HCl at 0.1 V s⁻¹.

TABLE 1: Cyclic Voltammetric Charge Values of CoHCF- and CoHCF + CTAB-modified electrodes in 0.1 M KCl + 0.1 M HCl solution (Pt Area = 2 cm²)

scan rate (V/s)	CoHCF		CoHCF + CTAB		Q_a/Q_c
	Q_a (mC cm ⁻²)	Q_c (mC cm ⁻²)	Q_a (mC cm ⁻²)	Q_c (mC cm ⁻²)	
0.02	2.03	2.04	2.31	2.38	0.97
0.04	2.10	2.10	2.14	2.17	1.10
0.08	1.31	1.32	1.92	1.93	0.99
0.10	1.38	1.38	1.99	2.00	0.99
0.12	1.25	1.25	1.82	1.83	0.99
0.14	1.27	1.27	1.90	1.91	0.99
0.16	1.21	1.21	1.84	1.87	0.98
0.18	1.17	1.17	1.80	1.82	0.98
0.20	1.16	1.15	1.78	1.79	0.99

critical micelle concentration (cmc) in the medium of our interest, and the optimal beneficial effects of CTAB are observed only at this concentration. Figure 2 depicts the response of CoHCF + CTAB-modified electrode in 0.1 M KCl + 0.1 M HCl. In this case too as in the case without CTAB, the anodic peak a_1 and the cathodic peak c_1 appear at about 0.45 and 0.3 V, respectively (at less-positive potentials). At the second redox center, at more-positive potentials, an anodic wave appears at ~ 0.58 V and its corresponding cathodic peak appears at ~ 0.5 V. There appears an additional prewave on the anodic side before a_1 , the origin of which is not clear at the moment.

At a glance, one can notice the great enhancement of the currents at the first redox center, a_1c_1 , due to the addition of CTAB as compared to the case without CTAB. It can also be seen that CTAB has hardly influenced the second redox center, a_2c_2 . Thus, as in the case of PB films,^{19,20} CTAB has enhanced the currents at the first redox center a_1c_1 alone at less-positive potentials and has not altered much the currents at the second redox center a_2c_2 at more-positive potentials. The improved resolution of the surface redox processes can also be noticed in case of the CV obtained with the addition of the surfactant. The film showed improved stability toward potential cycling in pure supporting electrolyte, and no reduction in peak current was noticed up to 125 cycles, and beyond that the percentage of reduction in peak current was less compared to non-CTAB films.

A comparison of potential values is not attempted, because they are not influenced because of the addition of CTAB. Table 1 gives the values of total charge at different scan rates on the anodic side and values of total charge at different scan rates on

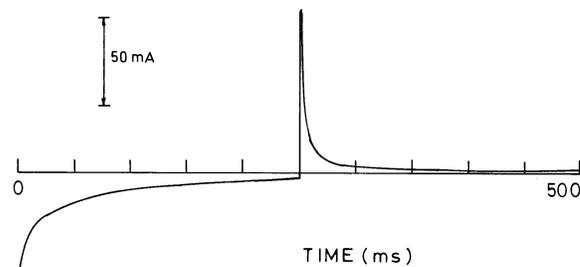


Figure 3. Current-time transients for CoHCF film in 0.1 M KCl + 0.1 M HCl. Potential step = 0–0.8 V and back to 0 V. Pulse width = 250 ms.

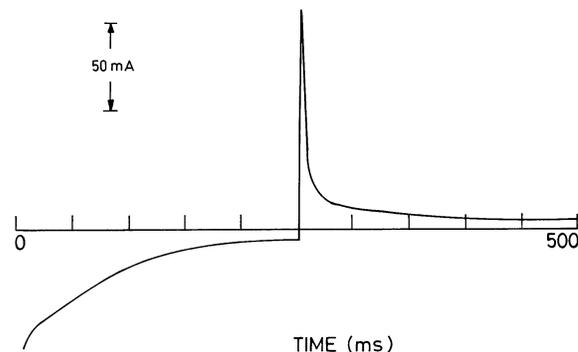


Figure 4. Current-time transients for CoHCF + CTAB film in 0.1 M KCl + 0.1 M HCl. Potential step = 0–0.8 V and back to 0 V. Pulse width = 250 ms.

the cathodic side pertaining to films of CoHCF formed both in the presence and in the absence of CTAB. The total charge at anodic and cathodic sides does not show a clear trend of decrease with increase in scan rate and associated with uncertainties. Comparison of peak currents is not attempted because of uncertainties involved in their measurement in the CV's as described. The Q_a/Q_c ratio is unity at all scan rates in both cases of films on the electrodes, that is, formed both in the presence and in the absence of CTAB. Enhanced anodic and cathodic charges due to CTAB addition are manifested at all scan rates.

Under our experimental conditions, no distinct electrochromism of CoHCF films in KCl could be observed, irrespective of whether the films are prepared in the presence or absence of CTAB. This may be because the film is too thin to exhibit visual color changes during redox cycling, and detailed spectrophotometric studies on CoHCF surface films of various thicknesses in the presence and absence of CTAB are in progress and will be reported in a future communication.

3.2. Current-Time Transients. *a. In KCl Supporting Electrolyte.* Current-time ($i-t$) transients were recorded at pulse widths of 250 ms in 0.1 M KCl + 0.1 M HCl for CoHCF film prepared in the absence of CTAB (shown in Figure 3). The corresponding $i-t$ transient (Figure 4) obtained for film prepared with the addition of CTAB revealed that the peak currents and the charge under the peaks of anodic and cathodic $i-t$ transients are not identical. In the presence of CTAB, the CoHCF film takes considerably longer time to reach the steady-state value. The rate of decay of current is considerably slower as compared to the case without CTAB, thereby showing the influence of CTAB on the kinetic rate of the charge-transfer reaction.

b. In NaCl Supporting Electrolyte. Unlike in KCl, the CV response of CoHCF film in 0.1 M NaCl gives two distinct redox centers as shown in Figure 5a,b, which are obtained for films formed without and with CTAB, respectively. For this reason, $i-t$ transients are obtained pertaining to both redox centers in

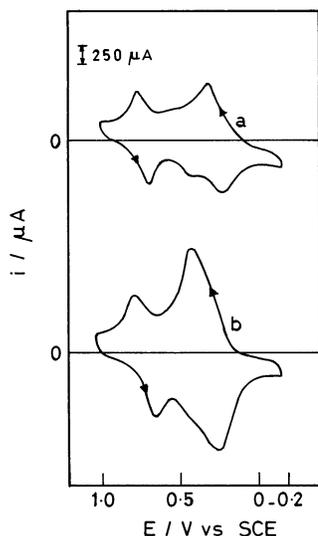


Figure 5. CV response of (a) a CoHCF-modified electrode and (b) a CoHCF + CTAB-modified electrode in 0.1 M NaCl.

this case. Current–time transients are recorded at a pulse width of 500 ms in 0.1 M NaCl for CoHCF film prepared in the absence of CTAB for the redox centers at 0–650 mV and 650–1000 mV. In the presence of CTAB, the CoHCF film takes considerably longer time to reach the steady-state value, as it does in KCl medium. The $i-t$ transients are similar looking and are not reproduced here, instead an example of a chronocoulometric curve for (a) CoHCF in 0.1 M NaCl and (b) CoHCF + CTAB in 0.1 M NaCl is given in Figure 6.

3.3. Chronocoulometric Studies. *a. In KCl Supporting Electrolyte.* By double potential step chronocoulometry, diffusion coefficients for both oxidation and reduction processes are computed for CoHCF films prepared in the absence and presence of CTAB in a supporting electrolyte of 0.1 M KCl + 0.1 M HCl. Diffusion coefficient (D) values at various pulse widths are calculated by using the Cottrell equation,²⁶

$$Q = \frac{2nFAD^{1/2} C_0 t^{1/2}}{\pi^{1/2}}$$

where the symbols have their usual meaning. The C_0 value used in the calculation is 6.26×10^{-3} mol/cm³^{27,28} assuming the unit cell dimensions for CoHCF to be similar to those of FeHCF (Prussian blue).²⁹ The slope values provided by the instrument during chronocoulometric studies at various pulse widths for both the types of films in 0.1 M KCl + 0.1 M HCl are used in the computation of diffusion coefficient values. As can be seen from Table 2, the diffusion coefficient values are too low, and the reason for the same is attributed to the assumption made in the value of the concentration of redox centers based on unit cell dimensions. The assumed value is most likely too high because the film is granular and the assumption made on the basis of unit cell dimension will hold good only if a single crystal is available.

Chronocoulometric studies show that at the same potential step (0–800 mV) increase in pulse width increases D values (Table 2) for oxidation and reduction processes of both CoHCF and CoHCF + CTAB. For the same pulse width employed, the diffusion coefficient value of CoHCF + CTAB film is about 2 times that of CoHCF film for the oxidation process and about 5 times for the reduction process. The diffusion coefficient value for the oxidation process is considerably greater than that for the reduction process at all pulse widths, irrespective of whether the film is formed in the presence or absence of CTAB.

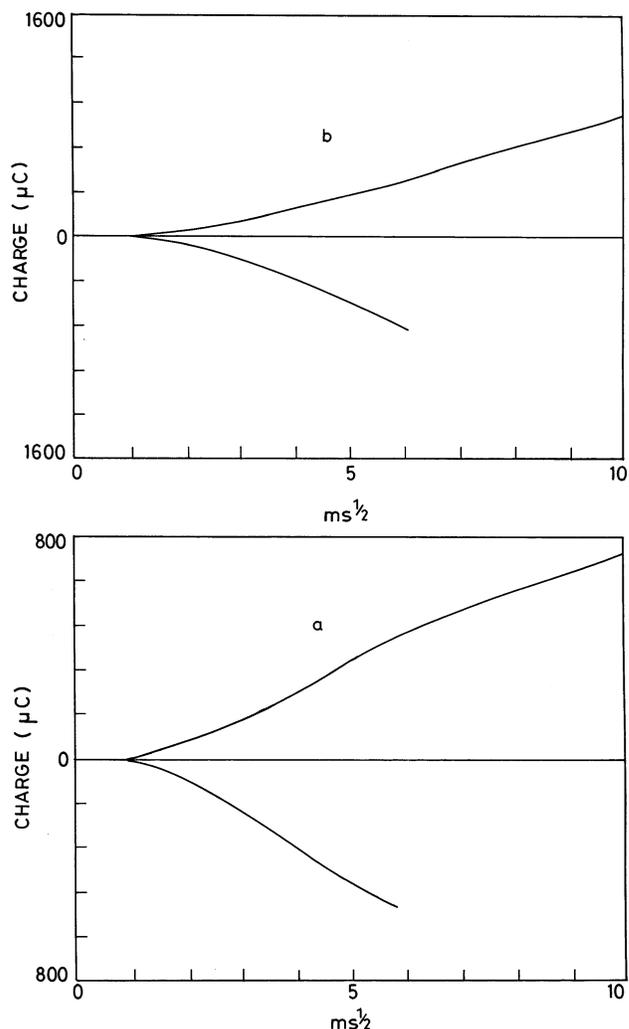


Figure 6. Chronocoulometric curve for (a) CoHCF and (b) CoHCF + CTAB film in 0.1 M NaCl.

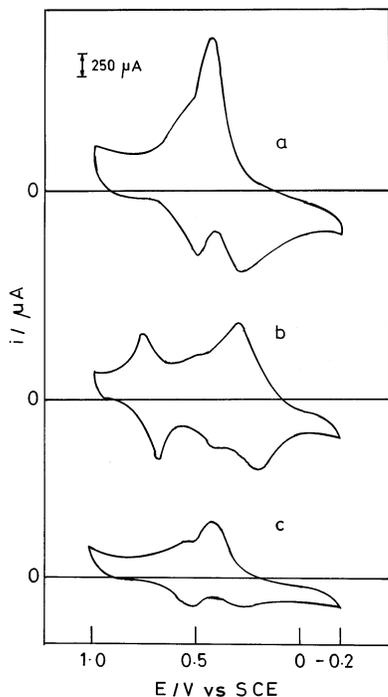
TABLE 2: Diffusion Coefficient Values at Various Time Scales Obtained from Double Potential Step Chronocoulometric Experiments (Pt Area = 2 cm²)

pulse width (ms)	CoHCF		CoHCF + CTAB	
	$D_{ox} \times 10^{-11}$ (cm ² /sec)	$D_R \times 10^{-11}$ (cm ² /sec)	$D_{ox} \times 10^{-11}$ (cm ² /sec)	$D_R \times 10^{-11}$ (cm ² /sec)
25	1.73	5.07	3.17	1.50
50	2.30	5.50	4.71	2.41
75	2.58	5.80	5.95	3.04
100	2.80	5.66	7.21	3.60

b. In NaCl Supporting Electrolyte. By double potential step chronocoulometry, diffusion coefficients for both oxidation and reduction processes are computed for CoHCF film prepared in the absence and presence of CTAB in the supporting electrolyte 0.1 M NaCl. The calculations are carried out as in the case of KCl supporting electrolyte by using the Cottrell equation. The values are obtained at the pulse width of 100 ms, however, for two potential regions (0–650 and 650–1000 mV), because there are two distinct redox centers in the CV response of CoHCF film in NaCl, whether the film is prepared in the presence or absence of CTAB. Table 3 gives the diffusion coefficient values. It can be seen from the table that the diffusion coefficient value of CoHCF + CTAB film is about 2 times that of CoHCF film for both oxidation and reduction processes for the potential range 0–650 mV. For the potential range 650–1000 mV also, the diffusion coefficient values for CoHCF + CTAB film are greater

TABLE 3: Diffusion Coefficient Values at the Pulse Width 100 ms Obtained from Double Potential Step Chronocoulometric Experiments (Pt Area = 2 cm²)

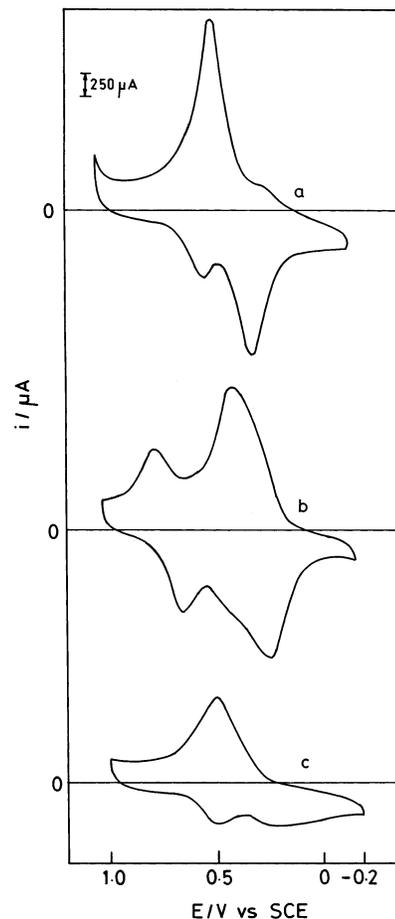
potential range (mV)	CoHCF		CoHCF + CTAB	
	$D_{\text{ox}} \times 10^{-11}$ (cm ² /sec)	$D_{\text{R}} \times 10^{-11}$ (cm ² /sec)	$D_{\text{ox}} \times 10^{-11}$ (cm ² /sec)	$D_{\text{R}} \times 10^{-11}$ (cm ² /sec)
0–650	0.32	0.75	0.70	0.16
650–1000	0.23	0.13	0.24	0.22

**Figure 7.** CV response of a CoHCF-modified electrode in (a) 0.1 M KCl, (b) 0.1 M NaCl, and (c) 0.1 M KCl, electrode being subjected to them in the given order.

than those of CoHCF film for both oxidation and reduction processes. While the diffusion coefficient value for the reduction process is greater than that for the oxidation process for both the types of films in the potential range 0–650 mV, it is the opposite observation in the potential range 650–1000 mV.

3.4. Voltammetric Studies in Other Supporting Electrolytes. The voltammetric, chronoamperometric, and chronocoulometric experimental reports so far pertain to the results obtained for CoHCF and CoHCF + CTAB films in KCl supporting electrolyte. The diffusion coefficient values obtained are due to the involvement of K⁺ ions in the charge-transfer process in addition to electron transfer, as represented in the equations given earlier. In view of the interesting ion-transport characteristics exhibited by metal hexacyanoferrates,^{30–33} especially CoHCF,^{13,14,35} it becomes all the more inevitable to study the ion-transport behavior of CoHCF + CTAB films in the presence of various alkali metal cations, such as Na⁺, Li⁺, and NH₄⁺, because there is always scope for interesting observations for these surface films in the presence of such cations. Such of those results are reported in the following while comparing the results obtained for CoHCF and CoHCF + CTAB films with the observations made in the presence of K⁺ ions, which serve as a reference point for comparison.

a. Voltammetric Studies in Sodium Chloride. Figure 7a shows the typical CV response of the CoHCF-modified electrode in 0.1 M KCl at the sweep rate of 0.1 V s⁻¹. When the electrode is thoroughly rinsed and its response is observed in 0.1 M NaCl, the cyclic voltammogram assumes the shape as in Figure 7b.

**Figure 8.** CV response of CoHCF + CTAB-modified electrode in (a) 0.1 M KCl, (b) 0.1 M NaCl, and (c) 0.1 M KCl, electrode being subjected to them in the given order.

The CV response is different in terms of redox location of peaks and their potentials as compared to those obtained in 0.1 M KCl. Unlike the case in KCl, CoHCF film gives two well-resolved predominant redox centers in NaCl, one at ~0.26 V and the other at ~0.73 V, and a redox wave in between. This response is similar to our earlier observations for the same system in NaCl medium.⁷ The observation is in tune with the earlier observation in NaCl made from this laboratory.⁶

When the electrode is again washed and its response is observed in 0.1 M KCl it reverts back to its original CV response (Figure 7 c), however, with greatly reduced peak currents on both anodic and cathodic sides (about 50% of the original response), the reason for which may be the partial solubilization due to hydration of CoHCF film by Na⁺ ions.³²

Figure 8 depicts the corresponding response of the CoHCF + CTAB-modified electrode in (a) 0.1 M KCl, (b) 0.1 M NaCl, and (c) again in 0.1 M KCl (recorded sequentially). The beneficial effects of CTAB, as described already, can be easily seen in Figure 8a. There is a total charge enhancement on both anodic and cathodic sides in comparison to the total charges obtained in case of film formed without CTAB, that is, as compared to 7a. Figure 8b shows the corresponding response of the thoroughly washed electrode in 0.1 M NaCl. There are two distinct redox centers in the CV of Figure 8b. The CV also depicts the enhanced charges at both of the centers in comparison to that obtained in absence of CTAB. The basic behavior of CoHCF film in 0.1 M NaCl remained the same, irrespective of whether the film is formed in the presence or absence of

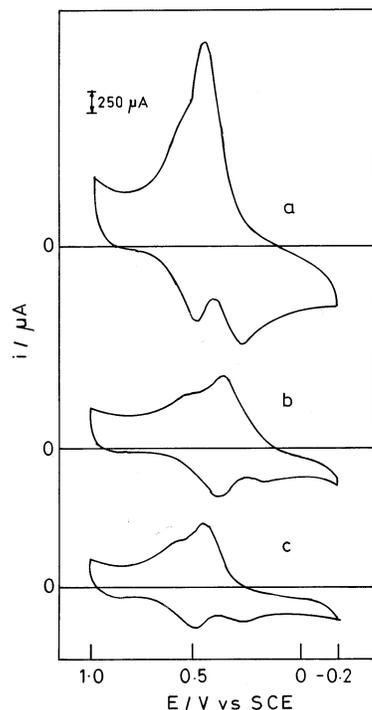


Figure 9. CV response of CoHCF-modified electrode in (a) 0.1 M KCl, (b) 0.1 M LiCl, and (c) 0.1 M KCl, electrode being subjected to them in the given order.

CTAB, that is, in both cases there are two redox centers and the peaks are broad.

When the electrode cycled in NaCl is again washed and its response observed in 0.1 M KCl, the normal response of CoHCF film in KCl is regained, however, with reduced charges (Figure 8c) as in the case without CTAB (Figure 7c).

b. Voltammetric Studies in Lithium Chloride. Figure 9a represents the typical CV response of the CoHCF-modified electrode in 0.1 M KCl at the scan rate of 0.1 V s^{-1} . When the electrode is well rinsed and its potential cycled in 0.1 M LiCl, a stabilized CV response as shown in Figure 9b is obtained. It is evident from the well-defined redox peaks that lithium ions have facile transport into the channels of CoHCF film. The fresh redox peaks appearing in the presence of 0.1 M LiCl are marked with reduced peak currents and corresponding Coulombic charges under the peaks, compared to their counterparts in 0.1 M KCl.

The CV response observed in 0.1 M LiCl is somewhat different from that obtained in 0.1 M KCl in terms of voltammetric redox peak potentials and the nature of peaks. There is one predominant anodic peak at about 0.49 V and a second anodic wave and two cathodic peaks at approximately 0.3 and 0.51 V in case of CV response of CoHCF film in 0.1 M KCl; on the other hand, two anodic peaks at about 0.39 and 0.57 V and two cathodic peaks at about 0.2 and 0.42 V are observed in the CV response obtained for CoHCF-modified electrode in 0.1 M LiCl. When the electrode is again washed and its CV response is observed in 0.1 M KCl, the CV response as shown in Figure 9c is obtained. It is seen that CoHCF film hardly regained its original KCl response; the reason may be attributed to its earlier potential cycling in LiCl. Degradation of CV response of CoHCF-modified electrode to about 50% in 0.1 M KCl, after having been subjected to potential cycling in LiCl, confirms the less-stable nature of CoHCF film in LiCl.

Figure 10 illustrates the corresponding response of the CoHCF + CTAB-modified electrode in (a) 0.1 M KCl, (b) 0.1 M LiCl,

and (c) 0.1 M KCl when the electrode is successively potential cycled in these media in this order. Figure 10a gives the enhanced form of the CV of CoHCF film formed in the presence of CTAB. The corresponding CV response of the film in 0.1 M LiCl is given by the Figure 10b.

The CV in Figure 10b resembles that in Figure 9b which is obtained in LiCl for CoHCF film formed in absence of CTAB, both of the cyclic voltammograms being marked with two sets of redox centers. In this case also, there is a total charge enhancement under the redox peaks with CoHCF + CTAB film in LiCl, in comparison to the total charge obtained with CoHCF film in LiCl.

Figure 10c depicts the subsequent CV response of well-rinsed electrode in 0.1 M KCl, which is the normal CV response of CoHCF film in KCl under our experimental conditions. Thus the film appears to have partially regained its KCl response after being subjected to potential cycling in LiCl. The regaining of KCl response in the case of film formed in the presence of CTAB is much more pronounced than that in the case of film formed without CTAB. As in the case of NiHCF film,²¹ the enhanced currents and charges in case of CoHCF film formed with CTAB can be seen in CVs 10a–c compared to the corresponding CVs 9a–c, which are obtained with CoHCF film formed without CTAB.

c. Voltammetric Studies in Ammonium Chloride. Figure 11a gives the CV response of CoHCF-modified electrode in 0.1 M KCl at a sweep rate of 0.1 V s^{-1} . Its corresponding response in 0.1 M NH_4Cl is depicted in Figure 11b (the electrode is rinsed well with distilled water before subjecting it to potential cycling in NH_4Cl). It is rather surprising to see that there are practically no features of faradic currents with the CoHCF film in NH_4Cl suggesting instability of CoHCF-modified electrode in NH_4Cl . This is in tune with the earlier observation made by other authors.²⁷ The reason for this may be either the blocking of pores in CoHCF by NH_4^+ or the solubility of CoHCF in the supporting electrolyte. The original response of the CoHCF-modified electrode in 0.1 M KCl could not be retraced when the same electrode is subjected to potential cycling in 0.1 M KCl after thorough washing with distilled water. However, one can notice some features of faradic process (Figure 11c).

The corresponding CV response of CoHCF + CTAB-modified electrode in 0.1 M KCl, 0.1 M NH_4Cl , and again in 0.1 M KCl are given in Figure 12a–c, respectively. The effect of CTAB manifests itself in the enhanced total charge in the CV obtained in KCl in Figure 12a in comparison to that in the CV obtained in KCl in Figure 11a.

Figure 12b representing the CV response of CoHCF + CTAB film in 0.1 M NH_4Cl is very similar to that given in Figure 11b, which represents the CV response of CoHCF film in 0.1 M NH_4Cl . Similarly, the CV in Figure 12c obtained with CoHCF + CTAB film in 0.1 M KCl (response obtained after cycling in 0.1 M NH_4Cl) is similar to the CV in Figure 11c obtained with CoHCF film in 0.1 M KCl. These observations indicate that there is no significant influence of CTAB on the behavior of CoHCF film in 0.1 M NH_4Cl .

d. Comparative Study of the Behavior of CoHCF and CoHCF + CTAB Modified Electrodes in Different Supporting Electrolytes. Among the supporting electrolytes studied, NaCl gave two well-defined redox centers with CoHCF film prepared both in the presence and absence of CTAB. However, the film formed in the presence of CTAB has one of the redox centers enhanced greatly (the redox center at less-positive potentials) with respect to peak current value. CoHCF film could not give redox peaks in NH_4Cl , even if it is prepared in the presence of CTAB. Li^+

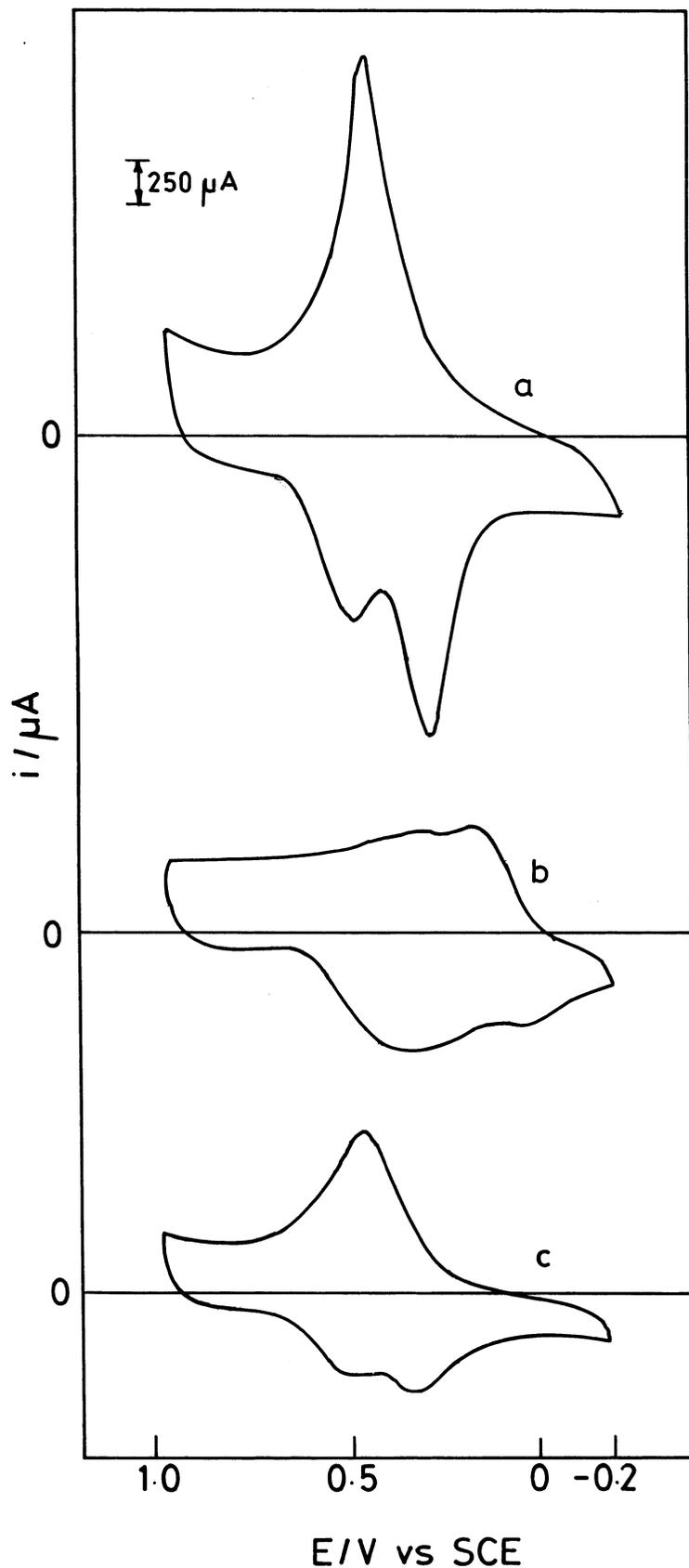


Figure 10. CV response of CoHCF + CTAB-modified electrode in (a) 0.1 M KCl, (b) 0.1 M LiCl, and (c) 0.1 M KCl, electrode being subjected to them in the given order.

ions are less-preferred compared to Na^+ and K^+ ions, as evidenced from the lesser charges obtained in LiCl compared to those in NaCl and KCl. From these observations, it becomes clear that CTAB does not affect the normal transport charac-

teristics of Na^+ , Li^+ , and NH_4^+ ions through the channels of CoHCF film. It is noted that the original KCl response of CoHCF film could not be retrieved after having the electrode subjected to potential cycling in NH_4Cl , irrespective of whether

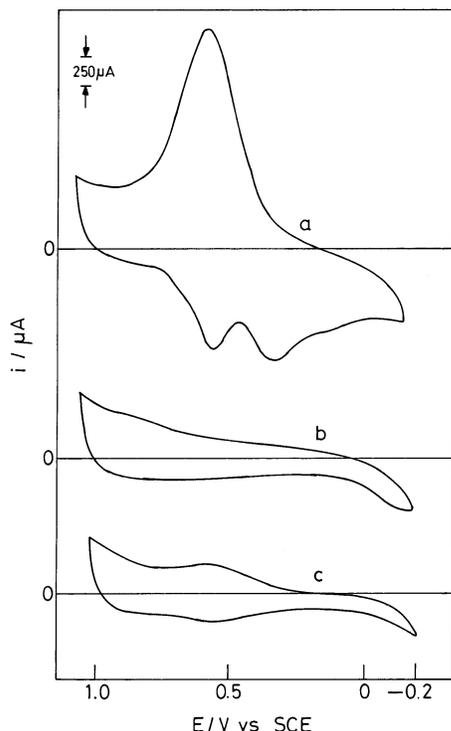


Figure 11. CV response of CoHCF-modified electrode in (a) 0.1 M KCl, (b) 0.1 M NH_4Cl , and (c) 0.1 M KCl, electrode being subjected to them in the given order.

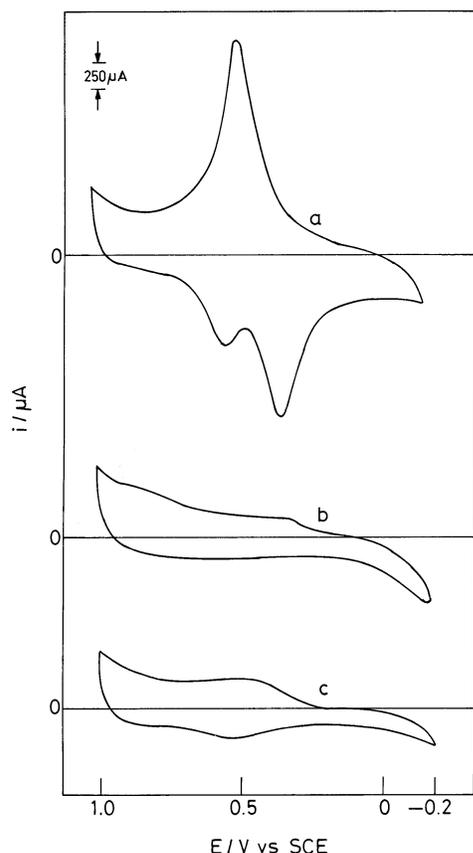


Figure 12. CV response of CoHCF + CTAB-modified electrode in (a) 0.1 M KCl, (b) 0.1 M NH_4Cl , and (c) 0.1 M KCl, electrode being subjected to them in the given order.

the film was formed without or with CTAB. This is a unique exception among the observations made with PB, NiHCF, and CoHCF films in different supporting electrolytes.^{21,34}

It is noticed in case of CoHCF film, as in the case of PB and NiHCF films,^{21,34} that CTAB does not seem to influence appreciably the channel size of CoHCF. It is inferred that CTAB present during the film formation has only current enhancement effect and does not alter the chemical composition of the film.

The surfactant adsorption onto the electrode surface has been modeled by several authors.^{35–37} It has been demonstrated³⁷ that on rough pyrolytic graphite (RPG) and glassy carbon (GC) surfaces the surfactant polar headgroups interact with hydrophilic groups at the surface leading to the formation of hemimicelles at the interface and, consequently, surfactant headgroups also face the solution. In the present work, we report that beneficial effects are noticed only at a specific concentration corresponding to the cmc of the surfactant CTAB. Therefore, it sounds logical to think that the observed effects are attributable to a specified orientation of the surfactant molecule on the electrode surface because there is evidence for the same from the modeling work done on surfactant adsorption on RPG and GC surfaces.^{35–37} At the same time, the fact that the nature of the electrode material can play a crucial role cannot be ignored.

4. Conclusion

The beneficial effects noticed due to the addition of CTAB during modification of electrode surfaces with cobalt hexacyanoferrate are manifested by increased peak current and charge and improved electrochemical reversibility. Unlike the case in KCl, CoHCF film formed either in the presence or in the absence of CTAB gives two well-resolved redox centers in NaCl. Current–time–transient studies showed that the rate of decay of current is considerably slower in the case of CoHCF film formed in the presence of CTAB as compared to the case without CTAB, both in KCl and in NaCl supporting electrolytes, which showed the influence of CTAB on the kinetic rate of the charge-transfer reaction. For the same pulse width employed, the diffusion coefficient value of CoHCF + CTAB film is always greater than that of CoHCF film both in KCl and in NaCl supporting electrolytes. Observation of behavior of CoHCF film 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 CTAB presence during the film formation has only catalytic effect and does not alter the chemical composition of the film.

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