

Surfactant effects on mediated electrocatalytic dechlorination of allylchloride

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Abstract

The effect of tetradecyltrimethylammonium bromide (TDTAB) on (1) the reductive electrochemistry of $[\text{Co}(\text{bpy})_3]^{2+}$ ion to $[\text{Co}(\text{bpy})_3]^+$, and (2) the $[\text{Co}(\text{bpy})_3]^{2+}$ -mediated electrocatalytic dechlorination of allylchloride has been studied in aqueous 0.1 M KBr solution. TDTAB micellar aggregates strongly stabilise the $1+$ complex against chemical decomposition, and also deeply activate it to substantially mediate the electrocatalytic dechlorination of allylchloride. The second order rate constant of the reaction between the micellar bound $1+$ complex and allylchloride, estimated by cyclic voltammetry under the conditions of pseudo first order kinetics, however, varies with substrate concentration. Cetyltrimethylammonium bromide (CTAB), on the other hand, gives a uniform value for the second order rate constant, but with reduced catalytic efficiency than TDTAB. The results suggest that the mediated dechlorination reaction is sensitive to the nature of the surfactant aggregates, and emphasise the need for further work on surfactant microstructures and the underlying physical processes. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Surfactant; Micelles; Electrocatalysis; Organic pollutants; Mediator

1. Introduction

Growing environmental awareness and concern have created a need to intensively search for safer disposal of organic pollutants, which are mostly alkyl/aryl chloro compounds. For disposal of these toxic materials, various degradation techniques, some as advanced technology and some at the explanatory stage, have been reported so far [1,2]: these studies include incineration, reaction with active metals such as sodium and potassium, high temperature hydrogenation, nucleophilic substitution of chlorine by hydroxide in the presence of polyethylene glycols, photo-chemical destruction using UV radiation to

cleave C–Cl bonds, photolysis in combination with hydrogen peroxide or ozone that provide a source of hydroxyl radicals for attack on the chlorinated substrates, etc. Electrochemical reductive dehalogenation is yet another method employed in recent times with proven capabilities [3].

Both direct [4–6] and indirect [7–10] electrochemical methods have been used for dehalogenation studies. However, as direct electrochemical methods require higher overvoltage to reduce the organic halides, efforts have been made to decrease the overvoltage for the C–Cl bond reduction. One approach is to catalyse the electron transfer reaction either by modifying the electrode surface [7,8] or by electrogenerating catalyst for homogeneous reaction [4,9,10]. In the latter case, namely indirect electrocatalysis, the idea is to add an oxidised form of a reversible

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redox couple to a solution containing the chlorinated substrate. At the potential characteristic for that redox couple but lower than the potential necessary for direct reduction of the substrate, the electrogenerated reduced form of the mediator transfers electrons from the electrode to the chlorinated substrate in the vicinity of the electrode surface. However, the one problem that is generally encountered in these indirect electrocatalytic reductions is that the non-polar organohalides are not soluble in water, and hence non-aqueous solvents, which are toxic and expensive, are often used.

In recent times, electrocatalytic dehalogenation of non-polar organohalides has been successfully achieved in aqueous media with the aid of surfactants. Rusling et al. [11–13] have extensively studied the destruction of organohalide pollutants, such as 4-bromobiphenyl, allylchloride, 4,4'-dichlorobiphenyl, PCB mixtures, and 4,4'-dibromobiphenyl, using a variety of organic and inorganic mediators, e.g. 9-phenylanthracene [11], $[\text{Co}(\text{bpy})_3]^{2+}$ (where bpy is 2,2'-bipyridine) [12], zinc phthalocyanine [13], etc. in aqueous solutions of various surfactants at different electrodes, viz. Hg, glassy carbon, pyrolytic graphite and clay-modified carbon electrodes. Anionic surfactant sodiumdodecyl sulphate (SDS) and cationic surfactant cetyltrimethylammonium bromide (CTAB) have been used in these studies. As surfactants have the tendency to solubilise both mediator and substrate together, and provide higher local concentrations of reactants on the electrode, enhanced rates of electrocatalytic reactions with the introduction of surfactant have been observed in the above systems. Generally, higher reduction efficiency has been noticed for cationic surfactant compared to the anionic one.

In this paper, we present detailed electrochemical studies of the effect of a cationic surfactant, tetradecyltrimethylammonium bromide (TDTAB) of molecular formula $\text{C}_{17}\text{H}_{38}\text{BrN}$, towards the $[\text{Co}(\text{bpy})_3]^{2+}$ -mediated electrochemical reduction of allylchloride in aqueous 0.1 M KBr. The performance of TDTAB is compared with that of CTAB surfactant ($\text{C}_{19}\text{H}_{42}\text{BrN}$), which is most widely used as a cationic representative [14] because of its well-founded surfactant chemistry [15,16]. The catalytic dehalogenation of allylchloride by $[\text{Co}(\text{bpy})_3]^{2+}$ mediation is chosen for surfactant evaluation because this reaction has been used previously as a prototype reaction for the

investigation of SDS and CTAB surfactants [12]. Our present studies show that TDTAB has higher catalytic efficiency, but influences the kinetics of the mediated reduction quite differently compared to CTAB, although both surfactants are cationic in nature. Cyclic voltammetry is used in the present work to examine the surfactant effect.

2. Experimental

TDTAB, CTAB and all other chemicals (KBr, $\text{CoCl}_2(7\text{H}_2\text{O})$, 2,2'-bipyridine and NaClO_4) were of A.R. grade and used as received. Allylchloride was distilled and used. Tris-cobalt(II) bipyridine complex was prepared following the literature procedure [17], and its formation was confirmed by UV–VIS spectroscopy (peaks at 296.2 and 242.2 nm). Solutions were made using charcoal-treated double-distilled water. Oxygen-free N_2 gas purified by passing it through acidified vanadous chloride solution containing Zn amalgam was used for deaeration. The temperature was maintained at $25 \pm 0.2^\circ\text{C}$ in all experiments.

Cyclic voltammetric experiments were carried out using a Wenking potentiostat (ST 72) coupled with a Wenking signal generator (VSG 83) and a Graph-tec X-Y-t recorder (WX 2300). The electrochemical cell was a conventional three-compartment glass cell. A platinum sheet and a dip type saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. A glassy carbon electrode (GCE) with geometric area of 0.198 cm^2 was used as a working electrode. The GCE was polished with increasingly fine grades of emery papers (2/0, 4/0, 6/0 Winning Emery, India) down to mirror finish, degreased with trichloroethylene, and thoroughly washed with copious amount of double-distilled water. The polished electrode was activated by electrochemical potential cycling method [18], which consisted of cycling its electrode potential between 500 and -1300 mV (SCE) for five times at a scan rate of 20 mV s^{-1} in deaerated 0.1 M KBr.

3. Results and discussion

3.1. Effect of TDTAB on the reduction of $[\text{Co}(\text{bpy})_3]^{2+}$ ion

The cyclic voltammograms (CV) of 2 mM of $[\text{Co}(\text{bpy})_3]^{2+}$ recorded at a scan rate (ν) 20 mV s^{-1} at

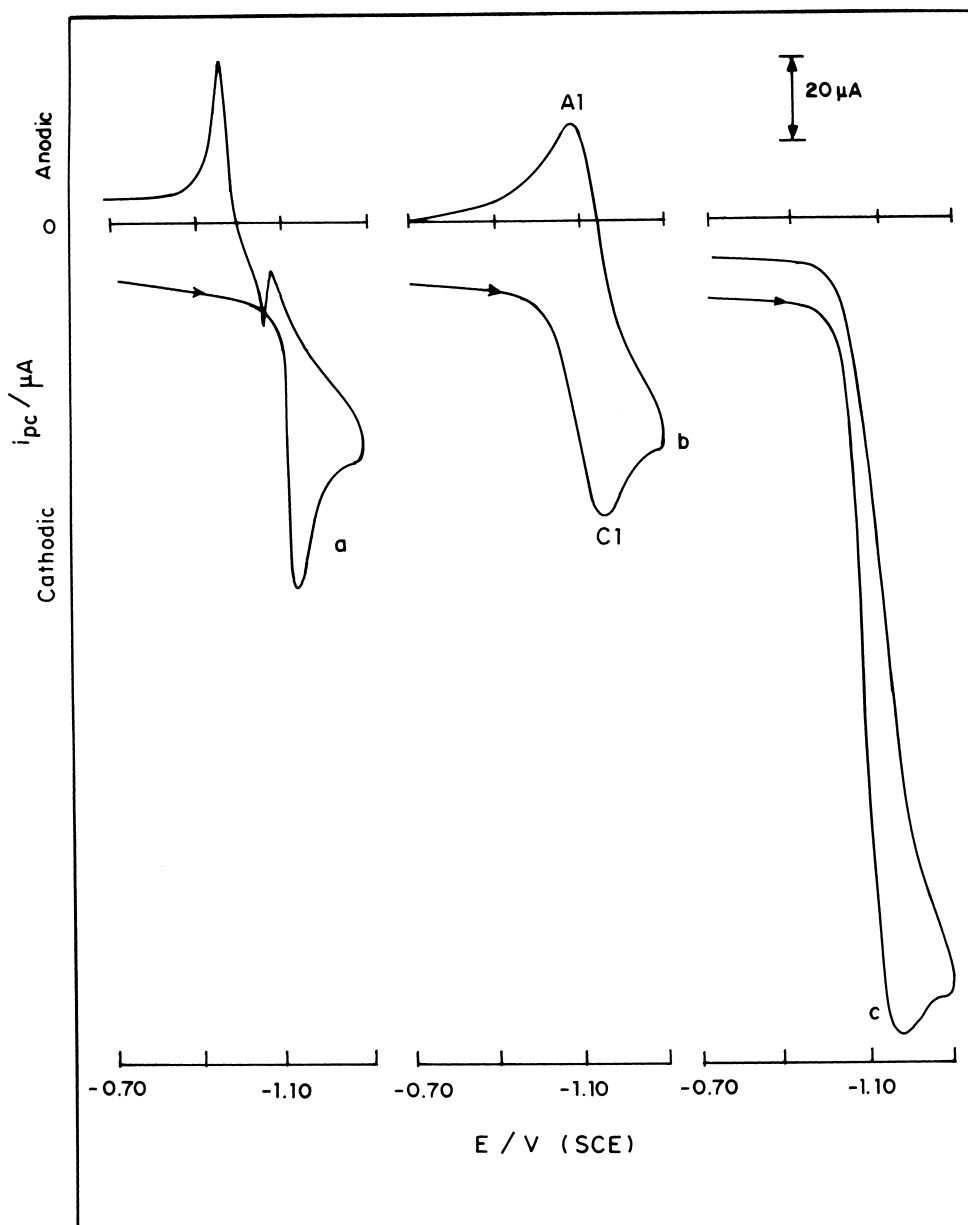
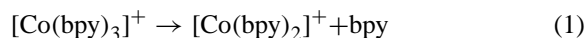


Fig. 1. Cyclic voltammograms recorded at a potential scan rate = 20 mV s^{-1} for $2 \text{ mM } [\text{Co}(\text{bpy})_3]^{2+}$ reduction at GCE in different aqueous solutions: (a) 0.1 M KBr ; (b) $a + 0.1 \text{ M TDTAB}$; (c) $b + 20 \text{ mM allylchloride}$.

a GCE in different experimental solutions are shown in Fig. 1. The voltammograms have been initiated from -500 mV (SCE) and the scan has been reversed at -1300 mV (SCE) . In the pure base electrolyte 0.1 M KBr , as shown in Fig. 1(a), $[\text{Co}(\text{bpy})_3]^{2+}$

gives a sharp cathodic peak at -1120 mV (SCE) , followed by two anodic peaks at -1120 and -1070 mV (SCE) in the reverse scan. The observed complicated redox behaviour of $[\text{Co}(\text{bpy})_3]^{2+}$ in 0.1 M KBr is due to the adsorption of the $2+$ complex and low

solubility of the product formed at the cathodic peak, viz. $[\text{Co}(\text{bpy})_3]^+$ complex [19]. The decomposition of the 1+ complex in aqueous solution cannot be ruled out as an additional factor for the occurrence of the multiple anodic peaks, since the tris-form of the 1+ complex is known to decompose to bis-form and the free ligand even in non-aqueous solvent acetonitrile [20,21].



Note that crossing of CV traces between the forward and reverse scans, signifying a series of chemical reactions occurring within the electrochemical time scales of the CV scan [22–25], provides experimental support for our proposal. However, further work related to this reaction mechanism is in progress.

The peak current of the cathodic peak varies linearly with $\nu^{1/2}$, as shown in Fig. 2(a), indicating that the reduction of Co(II) complex to Co(I) complex is under diffusion controlled. However, there appears a net intercept on the current axis, and this may be due to the electron transfer process complicated by the associated adsorption and chemical reaction.

The CV of $[\text{Co}(\text{bpy})_3]^{2+}$ in 0.1 M KBr in presence of 100 mM TDTAB shows dramatic changes, as illustrated in Fig. 1(b). The multiple anodic peaks are totally absent and there appears only one redox couple C1/A1. The anodic and cathodic peak potentials (E_{pa} and E_{pc}) for such voltammograms remain almost constant at -1150 and -1080 mV with increasing potential sweep rates up to ca. 80 mV s^{-1} . Anodic to cathodic peak separations (ΔE_{p}) are ca. 65 ± 5 mV at potential sweep rates up to ca. 140 mV s^{-1} , and the anodic to cathodic peak current ratios ($i_{\text{pa}}/i_{\text{pc}}$) are ca. 1.0 under these conditions. A plot of i_{pc} versus $\nu^{1/2}$ is linear and passes through origin, as shown in Fig. 2(b). Collectively, these features indicate a simple diffusion-controlled reversible one-electron transfer process to electro-active solution species. As the concentration of TDTAB is quite high, i.e. 100 mM, exceeding its cmc (3.5 mM [26]), the CV trace (Fig. 1(b)) reveals that the micellar-bound Co(II) metal complex diffuses towards electrode at slow rate and gets reduced at electrode surface reversibly. The absence of multiple anodic peaks in Fig. 1(b) is a clear indication that Co(I) complex is greatly stabilised in micellar environment, and it is not allowed to decompose when it is bound to TDTAB micelles. It may be

further concluded that all of the $[\text{Co}(\text{bpy})_3]^{2+}$ ions may be solubilised in micelles.

The diffusion-controlled electrochemical currents of micellar bound Co(II) metal complex is analysed further for the diffusion coefficient by using Randles–Sevcik equation [27],

$$i_{\text{pc}} = 0.4463nFA \left(\frac{nF}{RT} \right)^{1/2} D_{\text{M-Co(II)}}^{1/2} \nu^{1/2} c_{\text{Co(II)}} \quad (2)$$

where n is the number of electrons transferred per molecule of the reactant, F the Faraday constant, T the temperature (K), R the gas constant, $D_{\text{M-Co(II)}}$ the diffusion coefficient of the micellar bound $[\text{Co}(\text{bpy})_3]^{2+}$ species ($\text{cm}^2 \text{ s}^{-1}$), A the electrode area (cm^2), ν the potential sweep rate (V s^{-1}) and $c_{\text{Co(II)}}$ the concentration of the Co(II) complex (mol cm^{-3}). Slopes of the i_{pc} versus $\nu^{1/2}$ plot extrapolated to $\nu = 0$ give diffusion coefficient. With $n = 1$ and $A = 0.1932 \text{ cm}^2$, the $D_{\text{M-Co(II)}}$ for 2 mM $[\text{Co}(\text{bpy})_3]^{2+}$ with 100 mM TDTAB in solution has been calculated from curve (b) of Fig. 2 to be $7.93 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. Note that this value is smaller than the diffusion coefficient of 2 mM Co(II) complex in pure 0.1 M KBr base electrolyte with no surfactant in solution ($1.49 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, obtained from curve (a) of Fig. 2). The decrease in the diffusion coefficient value upon TDTAB addition agrees well with previously reported diffusion coefficient reductions of other species due to association with micellar assemblies [27].

In order to compare the influence of TDTAB surfactant with that of CTAB on the redox behaviour of $[\text{Co}(\text{bpy})_3]^{2+}$ ion in solution, similar CV experiments have been performed with 2 mM Co(II) complex in presence of 100 mM CTAB in 0.1 M KBr. The effect of CTAB is similar to that of TDTAB, with peaks C1 and A1 being observed. The i_{pc} versus $\nu^{1/2}$ data obtained for 2 mM of 2+ complex in 100 mM CTAB surfactant under similar experimental conditions are shown in Fig. 2(c). $D_{\text{M-Co(II)}}$ for CTAB bound- $[\text{Co}(\text{bpy})_3]^{2+}$ has been calculated to be $7.39 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, nearly same as that shown by TDTAB bound- $[\text{Co}(\text{bpy})_3]^{2+}$.

3.2. Effect of TDTAB on the mediated reduction of allylchloride

Allylchloride is not directly reduced on GCE in either 0.1 M KBr solution or potassium halide solution

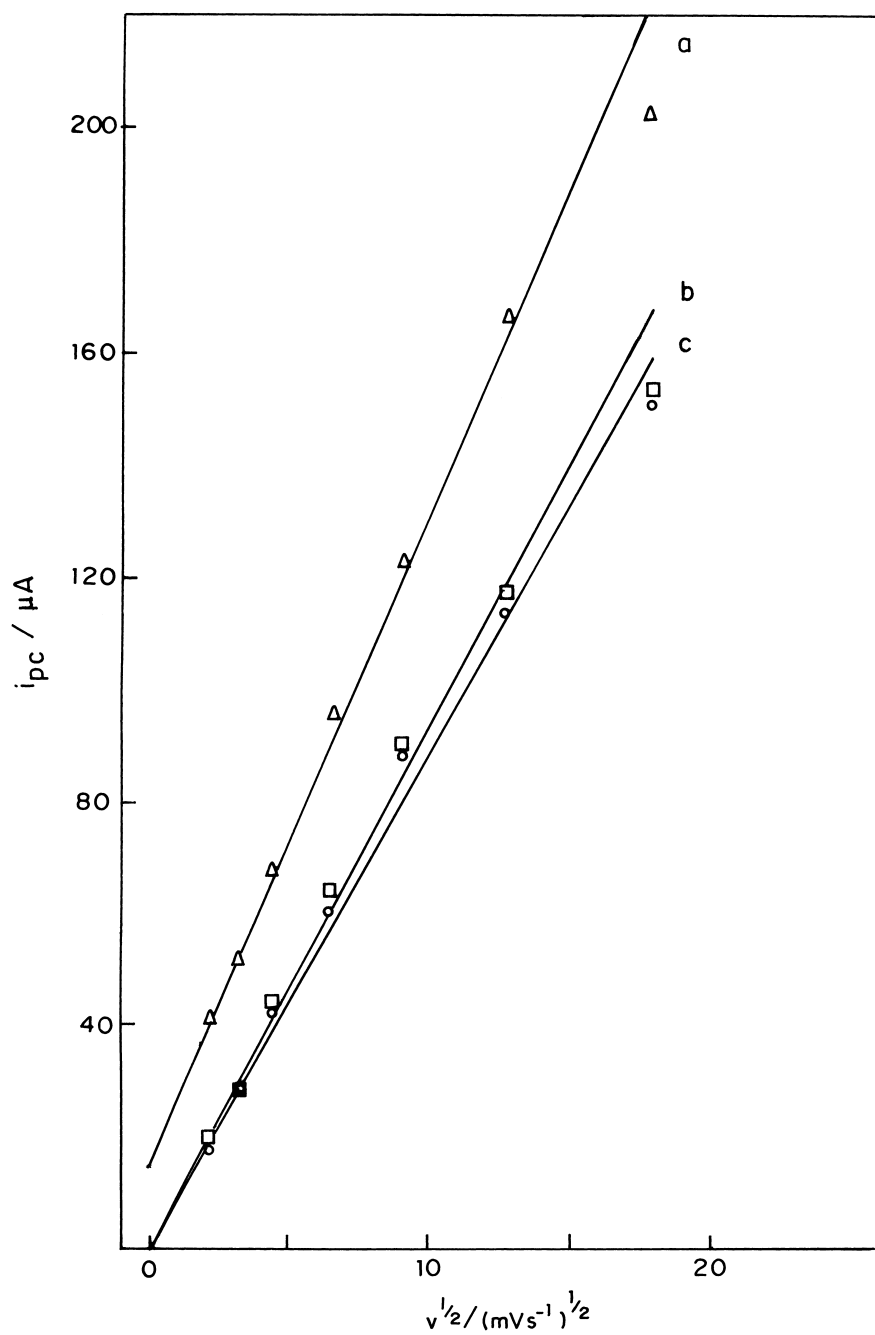
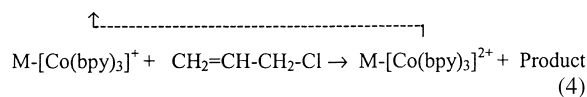
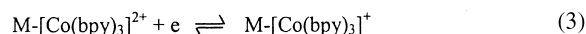


Fig. 2. Cathodic peak current vs. square root of scan rate plots for 2 mM $[\text{Co}(\text{bipy})_3]^{2+}$ reduction at GCE in different aqueous solutions: (a) 0.1 M KBr; (b) a + 0.1 M TDTAB; (c) a + 0.1 M CTAB.

containing 100 mM TDTAB. Also, $[\text{Co}(\text{bpy})_3]^{2+}$ is not able to electrocatalytically reduce allylchloride when the solution is devoid of the surfactant. By contrast, when allylchloride has been added to the solution containing both 2 mM $[\text{Co}(\text{bpy})_3]^{2+}$ and 100 mM TDTAB in 0.1 M KBr, in which micellar bound Co(II) ions with nearly perfect reversible redox electrochemistry are present (vide supra), the reduction peak C1 of micellar bound 2+ complex increases manifold while the anodic peak A1 eventually disappears, as illustrated in Fig. 1(c). This indicates that the overall process has become irreversible suggesting a subsequent chemical reaction involving the electrogenerated micellar bound- $[\text{Co}(\text{bpy})_3]^+$ and the allylchloride resulting in the regeneration of the parent (mediator) species. The reaction scheme for allylchloride reduction in the presence of TDTAB micellar bound Co(II) complex at the GCE under condition of homogeneous electrocatalysis can be represented as follows:



where M-X indicates micellar bound metal complex in solution. Electrocatalytic reduction of allylchloride by $[\text{Co}(\text{bpy})_3]^{2+}$ in acetonitrile [28] and in aqueous CTAB solution [12] yielded 1,5-hexadiene. Thus, a similar product can be assumed in TDTAB system.

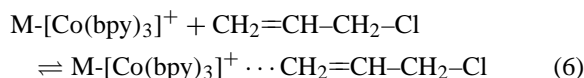
Rate constants for homogeneous electron transfer reactions have been measured by the cyclic voltammetric technique according to the method suggested by Saveant and Vianello [29] for catalytic current. The reaction has been carried out under pseudo first order conditions, i.e. with an excess of substrate. The experiments have been conducted by adding 0.01–0.12 ml of original solution of allylchloride to 25 ml of aqueous 0.1 M KBr solution containing 2 mM $[\text{Co}(\text{bpy})_3]^{2+}$ and 100 mM TDTAB. In this way, the mediator to substrate concentration ratio is in the range of 1:20–1:55. Voltammograms have been recorded at sweep rates of 5, 10, 20, 40, 80, 160, and 360 mV s^{-1} . The parameter measured is the peak current for the mediator in the absence (i_d) and the presence (i_{cat}) of substrate. Second order rate constants for the homogeneous reaction have been calculated using the following formula:

$$\frac{i_{\text{cat}}}{i_d} = \frac{1}{0.447} \left(\frac{RT}{nF} \right)^{1/2} \left(\frac{\sigma k c_z}{\nu} \right)^{1/2} \quad (5)$$

where c_z is the substrate concentration (mM), k the second order constant ($\text{M}^{-1} \text{s}^{-1}$) and σ the stoichiometric coefficient.

The i_{cat} measurements at different scan rates indicate that as the scan rate increases, the C1 peak current at -1150 mV increases and the current function, $i_{\text{cat}}/\nu^{1/2}$, decreases with $\log(\nu)$, as shown in Fig. 3(a) for TDTAB and Fig. 3(b) for CTAB solution. The latter behaviour testifies that the homogeneous chemical reaction between the $\text{M-}[\text{Co}(\text{bpy})_3]^+$ and allylchloride is the slowest step [29]. Note that the current function for the reduction of 2+ complex in aqueous 0.1 M KBr solution containing 0.1 M TDTAB or 0.1 M CTAB, in the absence of allylchloride in solution, is a straight line independent of ν (Fig. 3(c)) consistent with the fact that the Co(II)/Co(I) transition is nearly reversible in the TDTAB or CTAB micellar solution.

Fig. 4 shows that the plot of i_{cat}/i_d against $1/\nu^{1/2}$ is reasonably linear at low scan rates as expected accordingly to Eq. (5) for both 0.1 M TDTAB or 0.1 M CTAB in 0.1 M KBr solution containing 2 mM $[\text{Co}(\text{bpy})_3]^{2+}$ and 25 mM of allylchloride. Since, the ratio of cathodic peak current for the mediator in the presence of substrate to that in the absence of substrate is an indicator of catalytic efficiency at a given scan rate [30], Fig. 4 immediately reveals that TDTAB surfactant medium possesses higher efficiency towards the mediated reaction than CTAB system. Second order rate constant, k , has been calculated from the slope $(1/0.447)(RT/nF)^{1/2} (\sigma k c_z)^{1/2}$ of the above plots according to Eq. (5). The stoichiometric factor has been taken as one because 1 mol of 1+ complex is needed to reduce 1 mol of allylchloride. Table 1 gives the second order rate constant for both surfactants 0.1 M TDTAB and 0.1 M CTAB at different allylchloride concentrations. It can be seen that k decreases drastically with increase in substrate concentration in the presence of TDTAB surfactant, indicating certain chemical complications. Such behaviour is typical for a reaction which follows saturation kinetics in which a complex between the reactants is formed initially, e.g.



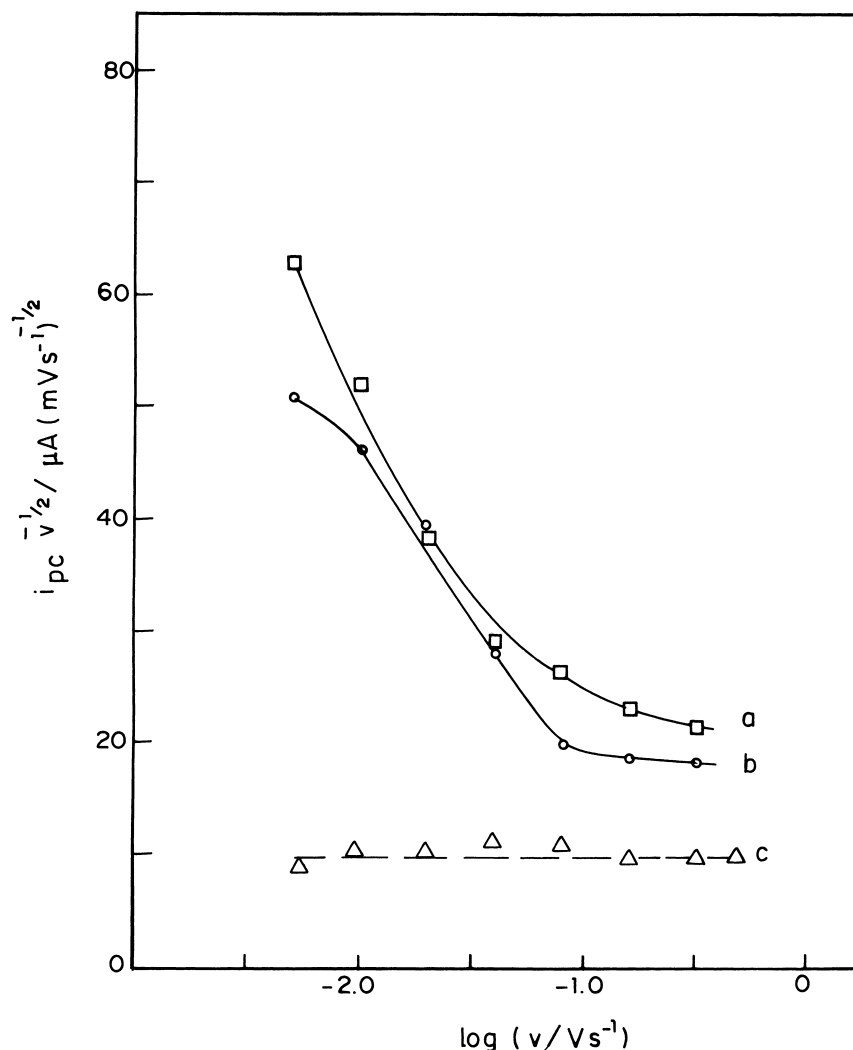
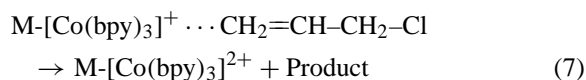


Fig. 3. Scan rate dependence of the ratio of voltammetric peak current i_{pc} to square root of the scan rate for 2 mM $[\text{Co}(\text{bipy})_3]^{2+}$ reduction at GCE in aqueous 0.1 M KBr + 25 mM of allylchloride: (a) 0.1 M TDTAB; (b) 0.1 M CTAB. Dotted line corresponds to 2+ ion reduction in 0.1 M KBr containing either TDTAB or CTAB with no substrate present.



By contrast, CTAB surfactant shows a constant value for k at all allylchloride concentrations, indicating that the net reaction is described well by the scheme in Eqs. (3) and (4).

The average k measured for CTAB/allylchloride/ $[\text{Co}(\text{bpy})_3]^{2+}$ system in the present work, i.e. $3.8 \pm 0.3 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$, is one order less than the

value $2.2 \pm 0.4 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ reported by Kamau and Rusling [12] for the above system under similar experimental conditions. The difference in k values can be explained as due to different electrode surface pretreatment methods adopted in the two studies (polishing followed by electrochemical activation and water wash in the present work versus alumina polishing and ultrasonic cleaning in the work of Kamau and Rusling [12]). It is well known that the surface pretreatment methods exert considerable influence on the

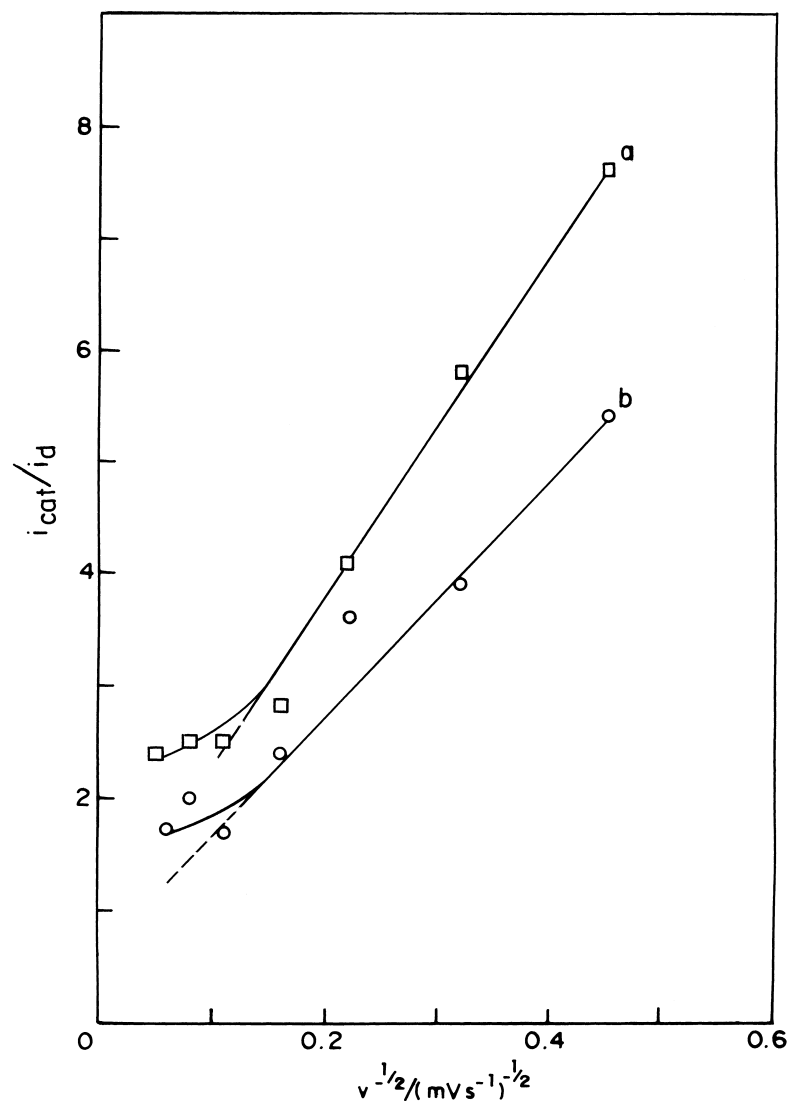


Fig. 4. Plot of catalytic current to peak current ratio as a function of $(1/(\text{scan rate})^{1/2})$ for 2 mM $[\text{Co}(\text{bpy})_3]^{2+}$ reduction on GCE in aqueous 0.1 M KBr + 25 mM allylchloride: (a) 0.1 M TDTAB; (b) 0.1 M CTAB.

electrochemical activity of carbon electrodes including GCE [18,31,32], and variations in pretreatment history can cause wide alterations in heterogeneous electron transfer rate constants, often by many orders of magnitude, for a particular redox system [33].

The observed difference in the behaviour of TDTAB and CTAB surfactants towards $\text{M}-[\text{Co}(\text{bpy})_3]^{2+}$ -mediated electrocatalytic reduction of allylchloride suggests that the influence of micellar aggregates on

the electrochemistry of a given mediated reaction cannot be predicted on the basis of simple electrostatic considerations, and micellar effects are strongly dependent on factors like micellar size, micellar structure, the extent of hydrophobic and coulombic interactions, the fraction of total electroactive mediator and substrate bound to micelles, etc. It is well known that these properties of the micelles essentially depend on the molecular structure of the surfactant

Table 1

Second order rate constant between allylchloride and electrogenerated micellar bound $[\text{Co}(\text{bpy})_3]^+$ in aqueous 0.1 M KBr + 0.1 M surfactant solution for different allylchloride concentrations^a

c_z (mM)	$k \times 10^{-1}$ ($\text{M}^{-1} \text{s}^{-1}$)	
	TDTAB	CTAB
20	12.0	4.1
25	7.0	3.6
35	5.4	4.1
45	3.2	3.4
55	1.9	3.8
Average 3.8 ± 0.3		

^a Concentration of $[\text{Co}(\text{bpy})_3]^{2+} = 2 \text{ mM}$.

[14]. Note that the molecular structure for TDTAB and CTAB differs by two CH_2 groups. The fact that $D_{\text{M-Co(II)}}$ is almost same for $[\text{Co}(\text{bpy})_3]^{2+}$ in TDTAB or CTAB solution (Fig. 2(a) and (b)) may be considered, as a first approximation, to indicate that the size of the micellar aggregates may be of similar order in both surfactants, assuming that the intermicellar interaction parameter [34] of TDTAB is same as that of CTAB. However, note that for CTAB in 0.1 M alkali bromide solutions, two types of micelles, i.e. spherical and larger rod-like aggregates have been reported to coexist on the basis of both light scattering data [15] and analysis of measured diffusion coefficients of CTAB-immobilised ferrocene [16]. Our preliminary diffusion coefficient measurements at a series of concentrations of $[\text{Co}(\text{bpy})_3]^{2+}$ in the range 0.05–5 mM in 0.1 M CTAB/0.1 M alkali bromide indicate that the measured diffusion coefficients decrease with increasing mediator concentration, which is a typical case of polydisperse system of micelles with the multiple binding sites for the solute per micelle [16]. Similar diffusion coefficient measurements for $[\text{Co}(\text{bpy})_3]^{2+}$ over the same concentration range in 0.1 M TDTAB/0.1 M alkali bromide indicate that $D_{\text{M-Co(II)}}$ is independent of mediator concentration, which signifies only one size distribution (i.e. a mono-disperse system) of micelles with a single binding site for the solute per micelle [16]. A positive confirmation of mono/polydispersity, evaluation of apparent binding parameters by the suggested curve fitting method [16], and their possible relation to the surfactant's catalytic behaviour are in progress, though at present we have no data to report.

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